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The Elements of

QUALITATIVE
CHEMICAL
ANALYSIS

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JULIUS STIEGLITZ

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With the author's
kindest regards
to Professor Jacques Loeb.

THE ELEMENTS
OF
QUALITATIVE CHEMICAL ANALYSIS

UNIV. OF

WITH

SPECIAL CONSIDERATION OF THE APPLICATION OF
THE LAWS OF EQUILIBRIUM AND OF THE
MODERN THEORIES OF SOLUTION

BY
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CHICAGO

THE KENT CHEMICAL LABORATORY OF THE
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R. M. R.

PRELIMINARY STATEMENT.

PART I of this book, which is in preparation, will contain the theoretical development of the subject of Qualitative Chemical Analysis as presented in the lectures of the author in the University of Chicago for the last thirteen years. It will include a discussion of the development and experimental foundations of the modern theories of solution; of the application of the laws of chemical and physical equilibrium to reactions used in analytical chemistry; of the theory of complex ions; and of the electric theory of oxidation and reduction; all with special attention to substantiating the theoretical treatment by lecture experiments.

Parts II and III, which are given in the present book, include the instructions for laboratory work introductory to systematic analysis and for systematic analysis. The attempt has been made, in particular, to bring the laboratory work, which otherwise follows the usual lines of instruction in systematic analysis, *also into closest relations to the development of the scientific foundations of analytical chemistry,* as presented in Part I. It is believed that the subject matter lends itself especially well to such a close interweaving of the two sides of the study, without any special loss of time to the student, and with the result, it is hoped, of a greatly increased interest on his part and an increased stimulus of the habit of scientific thought.

In the theoretical treatment the author is indebted to the original articles of van't Hoff, Arrhenius, Ostwald, Nernst, Bodlaender, Walker, etc., and, in particular also, to Ostwald's "Wissentschaftliche Grundlagen der Analytischen Chemie" which in 1894 first suggested the teaching of analytical chemistry along the lines followed here. For more extended reference on subjects of descriptive general chemistry, Alex. Smith's "General Inorganic Chemistry" and Remsen's "Inorganic Chemistry (Advanced)" are used. In the systematic analytical treatment, acknowledgment is due especially to Fresenius' Qualitative Chemical Analysis (frequent reference is made in the text to H. L. Wells' translation) and, for some special matters, to the work of W. A. Noyes of the University of Illinois, and of A. A. Noyes, of the Massachusetts Institute of Technology.

Special thanks are due to Professor Lauder W. Jones of the University of Cincinnati and to Dr. H. I. Schlesinger of the University of Chicago for their critical scrutiny and assistance in the preparation of the manuscript and correction of proof.

THE AUTHOR.

CHICAGO, May, 1908.

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QUALITATIVE ANALYSIS.

PART II

A. REACTIONS OF THE METAL IONS

THE FIRST OR ALKALI GROUP

Potassium, $K^{\cdot}$; *Sodium,* $Na^{\cdot}$; and *Ammonium* $(NH_4)^{\cdot}$, *Ions.*

1. Test aqueous solutions of each of the following compounds with neutral (violet) litmus paper, comparing the tints with that of a piece of the paper put into pure water:

(*a*) Potassium, sodium and ammonium hydroxide; test also the vapor above the solutions. Interpret the results.

(*b*) Sodium chloride, potassium carbonate. The interpretation of the results will be given in the "Aluminium Group."

2. (*a*) Add a little water to some calcium oxide in a small beaker to slake it, then add a few c.c. of ammonium chloride solution, and place a watch-crystal over the beaker with moist pieces of neutral and red litmus paper sticking to the lower side of the watch-crystal. Judging by 1 (*a*), would potassium and sodium salts react in the same way as ammonium chloride?

(*b*) Repeat the test in 2 (*a*), using lime-water in place of slaked lime. Compare (*a*) and (*b*). Which gives the better result? Which will give a more concentrated solution of ammonium hydroxide? Express by the equilibrium law applied to the dissociation of ammonium hydroxide into ammonia and water how the concentration will affect the test.

3. Heat a little of each of the following solid salts in a porcelain dish or crucible with the free flame, but below red heat: potassium, sodium and ammonium chlorides; sodium ammonium hydrogen phosphate. Observe which salts are volatile. If any fumes are given off, test them with moistened neutral litmus paper.

4. Get 1 c.c. of a 10 per cent solution of chloroplatinic acid from the storeroom.

(*a*) Add one drop of it to a drop each of solutions of potassium, sodium and ammonium chloride. Is there any difference shown in these tests?

(*b*) Repeat the tests, but first dilute the drop of each of the salt solutions with 10 c.c. of water. Why does this method of testing not prove conclusively the absence of the metals which according to (*a*) gave precipitates of chloroplatinates? Evaporate the solutions obtained in (*b*) to dryness in porcelain dishes over a water-bath, and add two or three *drops* of cold water to the contents of each dish.

Can we distinguish potassium from sodium salts by this test? Potassium from ammonium salts? According to the result in (*b*), what are the necessary conditions for applying this test successfully?

5. Heat a little of the following salts on the end of a clean (test?) platinum wire in the non-luminous flame:

(*a*) Potassium, sodium, ammonium chloride, each separately. Clean the wire until it gives no color to the flame, allow it to cool, touch it with the fingers and hold it again in the flame. What difference is there between the behavior of this minute trace of sodium chloride and the larger quantity of sodium chloride in the flame test?

(*b*) An intimate mixture (e.g., the mixed solutions) of approximately equal parts of potassium and sodium chloride.

(*c*) (*a*) and (*b*) may be repeated, the flames being examined with the aid of the spectroscope. Consult the instructor.

6. Using the results obtained in 1 to 5, devise a scheme of analysis for detecting potassium, sodium and ammonium salts in the presence of each other, without the use of the spectroscope. Show the scheme to the instructor or assistant and ask for an "unknown."

Characteristic of the alkali metals is that all their common salts are easily soluble in water. The hydroxides of sodium and potassium are very strong bases, the hydroxide of ammonium a weaker one, but still moderately strong. (Lecture.)

THE SECOND OR ALKALINE EARTH GROUP

Barium, $Ba^{\cdot\cdot}$; *Strontium*, $Sr^{\cdot\cdot}$; *Calcium*, $Ca^{\cdot\cdot}$;
Magnesium, $Mg^{\cdot\cdot}$, *Ions.*

(*Equilibrium. Ionization Constants. Solubility-Product Constants. Relative Solubility.*)

1. (*a*) Add a little water to some magnesium oxide or hydroxide and test the liquid over it with litmus paper.

(*b*) Shake some magnesium oxide with a little water and observe whether much of it dissolves. Add to a part of the mixture some hydrochloric or nitric acid (a slight effervescence would be due to the presence of a little magnesium carbonate in the oxide). What is formed? What class of oxides combine readily with acids? Give the equation.

(*c*) Add to another part of the mixture of solid magnesium oxide and water some sodium hydroxide. Is there any perceptible change? What does the result show as to any acid properties of magnesium hydroxide?

Barium, strontium and calcium hydroxide show the same typical behavior as magnesium hydroxide towards hydrochloric acid and sodium hydroxide. See table, p. 8, as to the relative solubilities of the hydroxides in water.

2. Test aqueous solutions of barium chloride and magnesium sulphate with neutral litmus. Does the test show whether we are dealing with salts of moderately strong or of weak bases? (Lecture on the Aluminium Group.)

3. Add to magnesium chloride solution some ammonium chloride, a little ammonia and then some sodium phosphate, added drop by drop. The precipitate is the *double* salt, magnesium ammonium phosphate, $\underline{Mg(NH_4)PO_4,6H_2O}$, which is used as a *characteristic test* to identify magnesium after the removal of all other metal ions excepting the alkalies.

4. (*a*) Add to some *concentrated* barium chloride solution (side-shelf) some *concentrated* sodium hydroxide solution, which should be as free as possible from carbonate (side-shelf). Note the crystalline appearance of the precipitated barium hydroxide.

(*b*) Add to another portion of the barium chloride some *concentrated* ammonium hydroxide solution (free from carbonate). (Note: on standing in the air, carbon dioxide is absorbed and traces of barium carbonate will form *from the surface downwards*.)

(*c*) To another portion of the barium chloride add some of the sodium hydroxide solution *diluted* with twenty parts of water.

(Traces of a flocculent precipitate are barium carbonate or ~~silicate~~, ~~due to slight impurities~~ in the alkaline solution.)

Taking (*a*) (*b*) and (*c*) together, is ammonium hydroxide as active or strong a base as sodium hydroxide?

5. (*a*) Add to 5 c.c. magnesium chloride, 5 c.c. water and ammonia as long as it will give a precipitate. Comparing 4 (*b*) and this result, which is less soluble in water, magnesium or barium hydroxide?

(*b*) Filter the solution from the magnesium hydroxide precipitated in (*a*), and add sodium phosphate to the filtrate. Did the ammonia precipitate the magnesium completely?

(*c*) Add to 5 c.c. magnesium chloride solution 5 c.c. ammonium chloride and then ammonia. Is a precipitate formed under these conditions? To understand this result carry out 6, 7, 8.

6. To 100 c.c. water add a few drops of phenolphthaleïn, and bring about 10 c.c. of the mixture into each of six test-tubes. To the first and second add a *drop* of sodium hydroxide. The resulting change in color is a characteristic test for the hydroxyl ion of bases, just as the litmus paper test is — but phenolphthaleïn is not as *sensitive* a test for the hydroxyl ion as litmus. Add to the deep red solution in the second test-tube a few crystals of sodium chloride and shake the mixture. Is there any marked change in color? To each of the other four tubes add a *drop* of ammonia and then add to the red liquid in one of the three, drop by drop, one or two c.c. of ammonium chloride solution, which should have been tested with litmus to ascertain that it has no acid reaction. What does the gradual change in color show in regard to the concentration and activity of the hydroxyl ion? When the solution has finally become colorless, test it with litmus to ascertain whether it is alkaline at all or whether the hydroxyl ions are only too few to affect phenolphthaleïn.

To one of the other test-tube solutions reddened by a drop of ammonia, add some solid ammonium nitrate or sulphate, to another add some sodium chloride. What conclusions will you draw as to the effect of a neutral *ammonium salt* on the strength of ammonium hydroxide as a base or its power to give hydroxyl ions? This is typical for the action of neutral salts of any *weak*

base on the free base itself[1] and for the action of neutral salts of a weak acid on the acidity of the free weak acid itself.[2] (Lectures.)

7. (*a*) Give the chemical and the mathematical equations for the equilibrium between ammonium hydroxide and its ions. In a solution containing 35 g. ammonium hydroxide (one gram-molecule) per liter conductivity measurements show that 0.4 per cent is ionized and 99.6 is non-ionized. What then are the concentrations of the ammonium and hydroxyl ions and of the non-ionized substance? Substitute these values in your equilibrium equation and calculate the ionization constant for ammonium hydroxide. In a solution containing 3.5 g. ammonium hydroxide per liter 1.4 per cent is ionized and 98.6 per cent non-ionized. What are the concentrations of the ammonium and hydroxyl ions and of the non-ionized substance in this solution? Calculate the constant from these data also.

(*b*) In a solution of 53.5 grams ammonium chloride (one gram-molecule) per liter, about 75 per cent of the salt is ionized. What change, then, would ammonium chloride produce if 53.5 grams were added to the first solution containing one gram-molecule of ammonium hydroxide per liter, as given in(*a*)? What would the total concentration of the ammonium ion now be? Why would equilibrium not be possible without further change? Calculate what the approximate concentration of the hydroxyl ion must be in this mixture when equilibrium is re-established.

(*c*) Why does sodium chloride not have the same decided effect on sodium hydroxide? (Lecture.)

8. (*a*) Give the equation for the "ion-product" or "solubility-product" constant[3] for magnesium hydroxide in its saturated solutions, in a condition of equilibrium in contact with the solid hydroxide. One liter of water dissolves 0.009 gram magnesium hydroxide; its molecular weight is 58; what is its concentration 0.009 gram per liter then, expressed in parts of a gram-molecule per liter? Considering the hydroxide to be *practically completely ionized*, what is the concentration of the magnesium ion? of the hydroxyl ion? Substitute these values in your solubility-product

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[1] Arrhenius, *Zeitschrift für Physikalische Chemie*, **2**, 287 (1888).

[2] *Vide* Küster, *Zeitschrift für Elektrochemie*, **4**, 110 (1897). Stieglitz, *American Chemical Journal*, **23**, 406 (1900).

[3] *Cf.* Stieglitz, *Journal of the American Chemical Society*, **30**, 946 (1908).

equation and calculate the solubility-product constant for the saturated solution.

(*b*) What must happen if we add some barium hydroxide solution to the saturated magnesium hydroxide solution, increasing the concentration of the hydroxyl ion? Test your conclusion by adding a few c.c. concentrated barium hydroxide (free from carbonate, side-shelf) to a saturated, clear solution of magnesium hydroxide.

(*c*) If to a solution of ammonium hydroxide containing one-tenth gram-molecule (3.5 grams) per liter, in which the concentration of the hydroxyl ion is .0014 (see 7 (*a*)), sufficient magnesium chloride were added to make the concentration of the magnesium ion equal to 0.100 (about 10 grams of the chloride per liter), — would magnesium hydroxide be precipitated, as judged by its solubility-product?[1] Would it still be precipitated, if by adding sufficient ammonium chloride (somewhat more than one gram-molecule) the ammonium ion should acquire a concentration of 1.00?

9. Add a few *drops* of ammonia to each of the following solutions and then repeat the experiments, adding a few c.c. of ammonium chloride to the solutions before adding any ammonia:

(*a*) Manganous chloride (zinc, nickelous, cobaltous, ferrous, cadmium salts and salts of many bivalent metal ions behave in the same way).

(*b*) Ferric chloride (aluminium and chromium salts behave in the same way).

According to these results, which hydroxides are more insoluble in water — those of (*a*) or (*b*)? If in doubt, add some ferric chloride to the mixture obtained in (*a*). The difference may be used for an almost quantitative separation of the two groups.

10. Magnesium salts do not color the Bunsen flame. The temperature of the electric spark is very much higher, and with its aid we can obtain the most sensitive and reliable qualitative test for magnesium, its spectrum showing with a very narrow slit of the spectroscope a very characteristic triple line in the green part of the spectrum; the triple line becomes a single line if the slit

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[1] The effect of the ammonium chloride formed should be neglected in the calculation; in rigorous calculations it would have to be considered. The direction of its effect is shown in what follows.

of the spectroscope is widened a very little. 0.0001 milligram of magnesium in a drop of liquid can readily be detected by this test without any inconvenience. (Instructor.)

11. Test a little of each of the chlorides of the other alkaline earths in the flame on a clean platinum wire.[1] The flame colorations may be examined with the spectroscope and the most characteristic lines noted.

12. (*a*) To a few c.c. each of solutions of barium, strontium, calcium and magnesium chloride, kept separate, add an equal amount of water, and a few drops of dilute sulphuric acid. Observe sharply any difference in the speed with which a precipitate may form in the different cases.

(*b*) To a few c.c. each of solutions of barium, strontium and calcium chloride, kept separate, add dilute sulphuric acid until no more precipitate is formed in each case, filter the solution and add to the filtrates four volumes of alcohol. What do the results show in regard to the relative solubilities of the sulphates in water?

(*c*) Mix a *drop* of each of the chloride solutions with about 10 c.c. water, and add a drop or two of dilute sulphuric acid. From your observations decide again the relative solubilities in water of the sulphates.

(*d*) To a solution of barium chloride add

(1) Some saturated solution of strontium sulphate.
(2) Some saturated solution of calcium sulphate.

Add the same reagents then to strontium and calcium chloride. What do these results show as to the relative solubilities of the sulphates?

(*e*) Mix 5 c.c. each of barium, strontium and calcium chlorides in a beaker, add an equal volume of water, heat the mixture to boiling, and, stirring vigorously, add, drop by drop, about 5 c.c. of a very dilute sulphuric acid prepared from one volume dilute acid and six volumes of water. Bring the precipitate on a very small filter, wash the filter and precipitate with hot water, until a few drops of the filtrate give no test for chlorides with silver nitrate. Then place a little of the precipitate on the *clean* platinum wire and heat it in the flame, after moistening it on the wire with a drop of hydrochloric acid. If the directions were carried out conscientiously a *single* color will appear in the flame. What does the experiment, taken in connection with (*a*), (*b*), (*c*) and (*d*), show as to the *order of precipitation* of analogous precipitates by the same reagent? This involves a general principle of great importance in analysis. What is the *limit of its reliability* — when will the more soluble precipitate appear first? To what fundamental law then is the principle subject? (Lecture.) Considering (*d*), what would the action of a solution of barium chloride be on some solid calcium sulphate? Even if some calcium sulphate were precipitated momentarily in (*e*) by a local excess (?) of sulphuric acid, would it remain as a precipitate in the presence of barium chloride? (Recall the lecture experiment on silver chromate and silver chloride.)

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[1] The wire is kept clean by keeping it in hydrochloric acid, or heating it with the acid, rinsing it with water and heating it in the flame; if it still colors the flame, the treatment is repeated.

13. Use a few c.c. of the solution of the chloride of each of the alkaline earths, including magnesium, for each of the following tests, the reagent to be added being given:

(*a*) Ammonium carbonate.
(*b*) Ammonium chloride and carbonate.
(*c*) Potassium chromate.
(*d*) Potassium dichromate.
(*e*) Ammonium oxalate.

Simply note the formation and non-formation of precipitates, and tabulate the results in an easily scanned form.

(*f*) *Dry* barium and strontium nitrate are insoluble in a mixture of absolute (anhydrous) alcohol and ether; calcium nitrate is soluble.

14. None of the precipitates is absolutely but only relatively insoluble in water. The following table gives the approximate solubilities of a few of the most important ones, as determined chiefly by Kohlrausch and Rose (*Zeitschrift für physik. Chemie*, XII, 234).

1 liter of water dissolves at ordinary temperature (18 degrees):

$BaSO_4$,	0.0027 gram	$BaCrO_4$,	0.004 gram	$BaCO_3$,	0.024 gram
$SrSO_4$,	0.1070 gram	$SrCrO_4$,	1.2 grams	$SrCO_3$,	0.011 gram
$CaSO_4$,	2.07 grams	$CaCrO_4$,	4.0 grams	$CaCO_3$,	0.014 gram

BaC_2O_4,	0.074 gram	$Ba(OH)_2$,	about	40 grams
SrC_2O_4,	0.045 gram	$Sr(OH)_2$,	"	10 grams
CaC_2O_4,	0.006 gram	$Ca(OH)_2$,	"	1.5 grams
		$Mg(OH)_2$,		0.009 gram

Which is the least soluble barium salt? strontium salt? calcium salt? Which reagent would be the most sensitive final test for each by a wet test? Will sulphuric acid precipitate barium, strontium or calcium from a solution of their carbonates? Can oxalic acid or ammonium oxalate precipitate barium, strontium or calcium from a solution of the sulphates? Test one of your conclusions.

Calculate the solubility-products for $BaSO_4$ and $SrSO_4$ from the above table. What is the limit for the relative concentrations of the barium and strontium ions for the precipitation of barium sulphate before strontium sulphate?

Characteristics of the Group of Alkaline Earth Metals. — They form strong bases, which are more or less soluble in water and are not precipitated by ammonia in the presence of ammonium chloride (difference from the aluminium group). Their sulphides are not precipitated from an aqueous solution (difference from the iron, copper, silver and arsenic groups). Their carbonates (excepting magnesium) and phosphates (including magnesium) are very insoluble in water (difference from the alkali group).

ANALYSIS OF THE ALKALINE EARTH GROUP.

There are various combinations of the reactions of the alkaline earth metals which may be used for a scheme of analysis of the group. The following method, Fresenius, *Qualitative Analysis*, p. 159, is considered the most accurate. Ask for an unknown and analyze it as follows:

(1) Add to the solution of the unknown 10–15 c.c. ammonium chloride, sufficient ammonia to make the reaction decidedly alkaline, and ammonium carbonate until no further precipitate is produced when ammonium carbonate is added to a little of a filtered sample of the liquid or to the clear supernatant liquid formed when the precipitate is allowed to settle. Heat the mixture gently and then collect any precipitated carbonate of barium, strontium and calcium (P) on a filter, using the filter pump to hasten the filtration (Instructor). In the filtrate (F) we may have traces of barium, strontium and calcium and all of the magnesium. Add a drop of dilute sulphuric acid to a small portion of the filtrate and observe whether a slight precipitate is formed in the course of a few minutes. (Very slight fine precipitates are often overlooked without experience. Consult the instructor as

to the best method for seeing one.) If a precipitate is formed, it can only be *barium* sulphate. (Consult the solubility table given above.)

Add to another portion of the above filtrate some ammonium oxalate. A slight precipitate would most likely be *calcium* oxalate, especially if it is formed in a few minutes; on longer standing difficultly soluble double oxalates of magnesium and ammonium are liable to be precipitated. If considerable magnesium is found (see below), the presence of calcium in this precipitate may be confirmed by allowing the precipitate to settle, decanting the liquid, washing the precipitate once by the same method, dissolving it in a drop of hydrochloric acid and a few drops of water and adding a drop of dilute sulphuric acid, and then four volumes of alcohol to the clear or filtered solution (see p. 7, 12 *b*). Alcohol would precipitate *calcium* sulphate. The possible trace of strontium in the filtrate (F) is neglected.

(2) The filtrate (F) having been tested for traces of barium and calcium, any traces are removed from the third main portion of (F) by means of a drop of dilute sulphuric acid and some ammonium oxalate, and the filtrate from the precipitated traces is tested for magnesium by means of ammonium phosphate. A *crystalline* precipitate would show the presence of *magnesium*. A *flocculent* precipitate, obtained in the course of a systematic analysis, is liable to be *aluminium* phosphate and is no proof of the presence of *magnesium*. The precipitate is allowed to settle, the liquid decanted and the precipitate treated with acetic acid; magnesium ammonium phosphate is dissolved, aluminium phosphate is not. The acetic acid solution is filtered from any residue and neutralized with ammonia; a crystalline precipitate is *magnesium* ammonium phosphate. (*Vide* p. 6 in regard to the spectroscopic test for magnesium.)

N.B. — If the filtrate (F) should have been allowed to stand over night before it is tested, carbonates containing magnesium are liable to crystallize out; any crystals are dissolved in acid and ammonia and ammonium phosphate added to the solution.

(3) The precipitated carbonates (P) (barium, strontium and calcium carbonate may be present) are placed in a porcelain dish and treated with dilute nitric acid, added drop by drop as long as there is any effervescence. The contents of the dish are brought

to dryness and the apparently dry nitrates heated in the dish on a wire gauze with a small flame, until no moisture collects in a cold beaker held a moment over the dish. *Shut off the flame,* pulverize the nitrates as soon and as rapidly as possible, add 5 to 10 c.c. of an anhydrous ether-alcohol mixture (care ! inflammable!), mix the liquid and solid thoroughly and filter the solution through a very small filter moistened with ether-alcohol, and wash the residue with a little more of the ether-alcohol mixture. The solution (**S**) contains any calcium nitrate, the residue (**R**), the nitrates of barium and strontium. *Any moisture present or allowed to be absorbed* will make strontium nitrate somewhat soluble and will vitiate the result.

To the solution (**S**), add a drop or two of dilute sulphuric acid, bring any precipitated calcium sulphate on a small filter, wash it with alcohol, dissolve it in water and add some ammonium oxalate to confirm *calcium.* (See the above table of solubilities.) If traces of strontium are to be looked for in (**S**) in very exact work, consult Fresenius, pp. 160–161.

(4) Dissolve the residue (**R**) in about 50 c.c. of water, heat the solution to boiling and add potassium dichromate until the solution is deeply colored. A precipitate would be *barium* chromate. After removing the solution by filtration, confirm the presence of *barium* by dissolving the precipitate in very little dilute hydrochloric acid and water and adding a drop of dilute sulphuric acid. A precipitate would be *barium* sulphate, which may be collected and also tested with the flame.

(5) To the filtrate from the barium chromate, ammonia and ammonium carbonate are added and the mixture is warmed. If a precipitate is formed it is most likely *strontium* carbonate, but may be calcium carbonate. Collect it on a filter, wash it, moisten it with hydrochloric acid and make the flame test for *strontium.* In case of doubt, match the color with that of a known strontium salt.

THE THIRD OR ALUMINIUM GROUP

Aluminium, Chromium, Ferric Iron.

Aluminium, $Al^{\cdot\cdot\cdot}$, and *Aluminate,* AlO'_2, *Ions.* (*Amphoteric Hydroxides; Hydrolysis of Salts.*)

1. Add sodium hydroxide drop by drop to two portions of a solution of aluminium sulphate until a heavy precipitate of aluminium hydroxide is formed in each.

(*a*) To the one precipitate add hydrochloric acid in excess. What is formed? What property of aluminium hydroxide is shown here? What ions must it form, which show this property? Give the equations.

(*b*) To the other precipitate add more sodium hydroxide, in excess. What property of aluminium hydroxide is shown here? What ions must it form which give it this property? What compound is formed in the solutions? Give the equations.

(*c*) Write the chemical and mathematical equilibrium equations in general terms for an aqueous solution of aluminium hydroxide (it is not absolutely insoluble), and its ions, for both forms of ionization, and show the effect of an addition of hydrochloric acid on *each* condition of equilibrium. Then show likewise the effect of an addition of sodium hydroxide on *each* condition of equilibrium.

2. Test a solution of aluminium chloride, nitrate or sulphate with neutral litmus paper. Does the result show that aluminium hydroxide must be a strong or a weak base? (Lectures.)

Sodium and potassium aluminate solutions react strongly alkaline. What does this fact prove as to the strength of aluminium hydroxide as an acid?

Note. — Apply the principle developed and discussed in the lectures, that a salt of a very weak base with a very weak acid must be quite largely decomposed by water, to show why aluminium hydroxide can be both base and acid without neutralizing itself to any appreciable extent. Show how its very small solubility in water is helpful in this decomposition. Apply the same principles to the results of the experiments in 3, 5, 6 (*a*).

3. Add ammonium hydroxide in moderate excess to a solution of aluminium nitrate or chloride. Is aluminium hydroxide readily soluble in excess of ammonia? Compare the result with that obtained in 1 (*b*) and explain the difference.

4. (*a*) Add sodium hydroxide gradually in moderate excess to a solution of an aluminium salt and use the clear solution of sodium aluminate for the following experiments:

(*b*) Add ammonia to a portion. Compare the result with 3 and explain the difference.

(*c*) Add hydrochloric acid very gradually to another portion until the solution is acid and then add ammonia in excess. Record

all your observations, explain the reactions, and give the equations.

5. Add about one c.c. ammonium sulphide to 5 or 6 c.c. of a solution of an aluminium salt. Note whether any gas is given off, bring the precipitate on a filter, wash it and the filter four or five times with water, and dissolve the precipitate then in hydrochloric acid. Is it a sulphide? Explain the result.

6. (*a*) Repeat 5, using sodium or ammonium carbonate in place of ammonium sulphide. Explain as before.

(*b*) Add to aluminium nitrate or chloride an excess of well-shaken milk of barium carbonate (side-shelf) — close the test-tube with the thumb and shake it carefully. When, after the addition of a little more barium carbonate, no more gas is given off on shaking the tube, filter the solution from the precipitate.

(*c*) Bring the precipitate into a porcelain dish, add a gram or two of solid barium hydroxide, the same amount of anhydrous sodium carbonate, and 20 c.c. of water, boil the mixture, and filter the hot solution. Acidify the filtrate with hydrochloric acid, boil it and add to the solution just enough ammonia to change the color of red litmus paper, and then two or three drops excess, and boil the mixture again. Observe whether a flocculent precipitate is formed. *This is a final test we use to identify aluminium.* The reactions used are the same as in 4 (*a*) and (*c*). Barium hydroxide and sodium carbonate are used in place of sodium hydroxide because the latter almost invariably contains alumina or silicic acid, which gives the same test with ammonia as aluminium salts do.

7. Add a drop of cobalt nitrate to a crystal of aluminium sulphate or nitrate in the cavity of a piece of charcoal and ignite the mixture with a blow-pipe (Instructor). The resulting blue compound (cobalt aluminate) is confirmative but not conclusive evidence of the presence of aluminium. There are some other blue cobalt salts which resist the action of heat — especially phosphates and silicates — and give a somewhat similar test.

8. Aluminium salts in solution give no characteristic flame or electric spark spectrum, but even in traces they affect the color of logwood extracts in a very characteristic fashion, and can be identified by studying the change of color, that is, the change of

the *absorption of light*, by means of the spectroscope. (See Vogel's *Spectral Analyse*, p. 202.) The test is particularly valuable because it can be made in the presence of many organic compounds which interfere with the ordinary tests for aluminium (see p. 58). Prepare a logwood decoction by boiling a chip with 20 c.c. water in a perfectly clean test-tube. Dilute the solution until the absorption band next to the sodium line appears in the spectroscope (Instructor), then add 1 c.c. of a solution of alum containing 1 milligram aluminium (Instructor), and note the change of the absorption. (*Vide* Vogel.)

Chromium Ion, $Cr^{\cdot\cdot\cdot}$.

1. Chromium forms two common oxides, chromic oxide, Cr_2O_3, and chromic acid anhydride, CrO_3. What is the valence of chromium in each? The hydroxide of the lower oxide is amphoteric but chiefly a base, like aluminium hydroxide; the hydroxide of the higher oxide is an acid. Salts of chromic oxide are green or violet, salts of chromic acid are yellow or red.

What kind of reaction would be used to convert a salt of chromic oxide into a chromate? For the reverse process?

(*a*) Fuse any chromium salt with some sodium carbonate and potassium chlorate on a porcelain lid and extract the cooled mass with water. What is the rôle of the chlorate in the fusion? Of the sodium carbonate? Add acetic acid and lead acetate to the aqueous extract. The precipitate is lead chromate. This is the chief *test* we use to *identify chromium.*

(*b*) Treat a little of a solution of a chromium salt with sufficient sodium carbonate to produce a precipitate and then add a *little* sodium peroxide (care!). Sodium chromate is formed. This is another *identification test* for *chromium.*

(*c*) Acidify a few c.c. of potassium chromate solution and pass hydrogen sulphide in *excess* into the solution. Filter the solution. What does the change of color show? (See pp. 45, 46, 55, and lectures on *oxidation* and *reduction*.)

2. Heat some sodium ammonium hydrogen phosphate (microcosmic salt) on the end of a platinum wire, add a minute fragment of a chromium compound to the clear bead and heat the mixture in the flame. (Refer to the lecture on the chemistry of the metaphosphate and borax beads.)

3. Use a solution of chromium chloride or sulphate for the same tests as given under 1 (*a*) and (*b*) for aluminium. After using the excess of sodium hydroxide according to 1 (*b*), heat the solution to boiling. What is the effect of heat on the ionization of water? What difference from aluminium is shown here? Can aluminium be separated from chromium by this means?

4. The reactions described for aluminium under 2, 5, 6 (*a*) and (*b*), but not 6 (*c*) are also given by chromium. Note should be made of these facts, but the experiments need not be made.

Ferric Ion, $Fe^{\cdots}$.

1. Iron forms two common oxides, ferrous oxide, FeO, giving salts resembling in general properties those of the next group, in which they will be included, and ferric oxide, Fe_2O_3, whose salts resemble more those of aluminium and chromium. They are, therefore, included in the aluminium group.

(*a*) What class of reagents must be used to convert ferrous salts into ferric? and *vice versa?*

(*b*) Dissolve part of a steel nail in hydrochloric acid, decant the solution, add a very few crystals of potassium chlorate and heat the mixture until no chlorine odor remains. Note the change of color. What is formed?

(*c*) Pass hydrogen sulphide in excess through a dilute solution of ferric chloride and filter the solution. Note the change of color of the solution. Heat a little of the precipitate on a glass rod. What is it? What is the reaction?

2. (*a*) Test a solution of ferric chloride with neutral litmus paper. What does the result show as to the strength of ferric hydroxide as a base?

(*b*) Add sodium carbonate gradually to the solution and note everything that occurs. The precipitate is chiefly ferric hydroxide. Explain its formation. What connection has the conclusion arrived at in (*a*) with the result of this test?

(*c*) Shake the solution of ferric chloride with an excess of barium carbonate suspended in water. Compare the result with (*b*) and compare it also with 6 (*b*) under "Aluminium" and 4 under "Chromium." *Aluminium, chromium and ferric chlorides or nitrates show this same behavior towards barium carbonate,* differing from the behavior of the corresponding salts of the metals of the next (ferrous) group. Barium carbonate is used, therefore, as a *group reagent* to separate the two groups from each other.

3. Add to ferric chloride solution some sodium hydroxide. Then add an excess of the alkali. Does the precipitate redissolve? Has ferric hydroxide sufficient acid properties to form a sodium salt in the presence of water? Compare it with aluminium hydroxide in this regard [Aluminium, 1 (*b*)] and with chromium hydroxide (Chromium, 3). Arrange the hydroxides in the order of decreasing acid properties and note the corresponding order of the atomic weights of the elements. Read in Smith, Remsen, or Ostwald on *ferrites* obtained in a dry way, which are metal salts of ferric hydroxide, $Me^{\cdot\cdot}(FeO_2)_2$.

4. Add to portions of a dilute solution of ferric chloride:

(*a*) Potassium ferrocyanide. The precipitate is Prussian-blue and gives one of the most sensitive tests for ferric iron.

(*b*) Potassium ferricyanide.

(*c*) Ammonium thiocyanate. This is the most sensitive test for ferric iron. Fresenius, p. 211, gives precautions for using it. Take a single drop of ferric chloride solution, add it to 200 c.c. of water and test a portion in a test-tube for iron with thiocyanate; if no color shows, add a few c.c. ether and shake the mixture and note the color of the ether layer.

5. Add to a *freshly prepared* solution of potassium ferricyanide:

(*a*) Ammonium thiocyanate. Add ether and shake the mixture. Explain the absence of any red color. Recall the lecture experiment on the migration of ferricyanide ions.

Add a few drops of concentrated hydrochloric acid to this mixture and shake it again with ether and note the appearance of a faint red tint against white paper. The explanation of this result will be given in the discussion of complex ions and their conditions of equilibrium (p. 30, 1 (*e*)).

(*b*) Potassium ferrocyanide (fresh solution).

(*c*) Ammonia.

6. Mix a good pinch of pulverized potassium ferrocyanide with an equal amount of dried, pulverized potassium *carbonate,* fuse the mixture in a test-tube held horizontally in the flame, until the whole mass has charred (*avoid inhaling any fumes of hydrocyanic acid through the course of this experiment*), then, after the tube has cooled a few seconds, plunge (Care!) the hot end of the test-tube into a

small beaker of water (50 c.c.); allow the alkali salts to dissolve and the iron and carbon to subside, decant the liquid, and wash the residue twice with hot water. Treat the residue with dilute hydrochloric acid to dissolve the iron, filter the solution and oxidize the ferrous salt with a few drops of bromine water and then add an excess of ammonium thiocyanate. If the experiment was carried out correctly, iron will be plainly indicated. Compare the result with 5 (*a*) and (*b*). The reactions are:

$$\begin{array}{ll} \mathrm{K_4Fe(CN)_6 + K_2CO_3} & \rightarrow \mathrm{FeCO_3 + 6KCN.} \\ \mathrm{FeCO_2} & \rightarrow \mathrm{FeO + CO_2.} \\ \mathrm{FeO + KCN} & \rightarrow \mathrm{KCNO + Fe, etc.} \end{array}$$

7. Test a little of an iron salt with the borax or metaphosphate bead in the oxidizing and the reducing zones of the Bunsen flame.

Characteristics of the Third or Aluminium Group. — The hydroxides are very weak bases, and do not form sulphides in the presence of water (difference from the ferrous, copper and arsenic groups). The hydroxides are very insoluble and are precipitated by ammonia, even in the presence of ammonium chloride (difference from the alkaline earth group, and from the ferrous group) and by barium carbonate (difference from the ferrous group).

An analysis of the group will be made together with the next group (p. 21).

The Fourth or Ferrous Group

Ferrous Iron, Nickel, Cobalt, Manganese and *Zinc.*

Group Reactions. — 1. (*a*) Test a solution of a nickelous salt with litmus. Is the hydroxide a very weak base?

(*b*) Add to the solution sodium carbonate. Does nickel form a carbonate stable in the presence of water? Cobaltous, ferrous, manganous, and zinc salts show the same behavior. Compare this result with the behavior of aluminium, chromium and ferric salts. Which are the stronger bases, the bivalent hydroxides of this group or the trivalent ones of the previous group? *Herein lies the chief and characteristic difference between the two groups, and their main group reactions are based on this contrast.*

2. (*a*) Treat nickelous *chloride* or *nitrate* with suspended barium carbonate and filter the solution. Is the nickel precipi-

tated? According to this result, which carbonate is less soluble in water, barium or nickel carbonate?

The same behavior is shown by ferrous, cobaltous, manganous and zinc chlorides or nitrates.

(*b*) Mix a little ferric *chloride* and nickelous *chloride*, and add to the mixture barium carbonate in excess. Filter and examine the color of the filtrate, concentrating the solution if necessary. This is the typical separation of the third and fourth groups from each other. (Lectures.)

(*c*) Treat nickelous *sulphate* with suspended barium carbonate and shake the mixture vigorously. Collect and wash the precipitate, dissolve it in dilute hydrochloric acid, and add ammonium sulphide to the solution. Is nickel carbonate precipitated from the sulphate solution by barium carbonate? Explain the difference in the result obtained in (*a*) and (*c*). May the sulphates be used in the separation of the third and fourth groups?

3. Recall the results of experiments 9 (*a*) and (*b*) under Magnesium (p. 6).

4. (*a*) Take solutions of the ferrous, nickelous, cobaltous, manganous and zinc salt and add to each some ammonium sulphide. Note the colors of the precipitates. Are sulphides or hydroxides precipitated? Make tests, if in doubt. Compare the results with the behavior of aluminium and chromium and correlate the facts with those obtained above in 1 (*b*).

(*b*) Pass hydrogen sulphide into each of the salt solutions.

(*c*) Acidify each solution with a few drops of hydrochloric acid and pass hydrogen sulphide into each one. *Herein lies the typical analytical difference between the ferrous group and the next groups, the silver-copper and arsenic groups.* (Lectures.)

In addition to these general group reactions of the salts of the metals of this group, which are used in separating the group from other groups, the characteristic reactions for separating them from each other and for identifying them must be studied.

Ferrous Ion, $Fe^{\cdot\cdot}$.

1. Add to a freshly prepared solution of ferrous ammonium sulphate a few drops of hydrochloric acid and a steel nail (to reduce any ferric salt present) and test it with: (*a*) potassium ferrocyanide; (*b*) potassium ferricyanide; (*c*) potassium thiocyanate. Com-

pare the results with those obtained with ferric salts in the analogous experiments. How would we recognize ferrous and ferric salts in the presence of each other?

2. Recall the metaphosphate and borax bead tests with iron salts. (See Ferric Iron, 7.)

Nickel, $Ni^{\cdot\cdot}$, AND *Cobalt,* $Co^{\cdot\cdot}$, *Ions.*

1. Test a *little* of a salt of each metal with the borax bead. Mix about equal parts of the salts and test the mixture with the borax bead.

2. Use a few c.c. of the solution of some nickel salt for each of the following tests, the reagent to be added being given. Then make the same tests with a cobalt salt and note all the results:

(*a*) An excess of sodium hydroxide. Have the hydroxides acid properties?

(*b*) An excess of ammonia.

(The chemistry of this reaction will be considered in the next group under Silver, 2.)

(*c*) An excess of ammonium sulphide. Filter the liquid and note the characteristic difference between nickel and cobalt, and compare the result with (*b*). This is an important reaction of *nickel* by means of which its presence is often most easily discovered.

3. Add to a nickel or cobalt salt solution:

(*a*) A few drops of hydrochloric acid and then hydrogen sulphide in excess.

(*b*) A few drops of ammonium sulphide. Decant the liquid from the precipitate and then add quite dilute hydrochloric acid to the precipitate.

What is there that is remarkable in the fact that (*a*) and (*b*) seem to lead to a *different* result? (Lecture.)

4. Test a nickel salt as follows, noting all the results, and then test a cobalt salt in the same way:

(*a*) Add an excess of sodium hydroxide and then bromine water. The black precipitates are nickelic hydroxide, $Ni(OH)_3$, and cobaltic hydroxide, $Co(OH)_3$.

(*b*) Add a solution of potassium cyanide *drop* by *drop* until the precipitate first formed has just redissolved, then add a few *drops* excess of the reagent. (*Note:* Great care must *always* be used in handling potassium cyanide, which is *a deadly poison*. Precautions are given on the reagent-bottle and *should be observed.*) Warm the solution, add 5 to 10 c.c. sodium hydroxide solution and an excess of bromine water. Heat the mixture. This reaction gives us the best method for determining *nickel* in the presence of cobalt. (See Ferric Iron, 5, and later under Copper, 1 (*c*), as to the effect of potassium cyanide in forming *complex ions* of characteristic stability. Lectures.)

(*c*) Add some acetic acid and a large *excess* of potassium nitrite and warm the solution. Cobalt salts give a precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$,Aq. This reaction gives us the best method for determining *cobalt* in the presence of much nickel.

Zinc Ion, $Zn^{\cdot\cdot}$.

1. Test a zinc salt with the borax bead. Heat some with a drop of cobalt nitrate on a piece of charcoal with the blow-pipe.

2. Add to a zinc salt solution gradually:

(*a*) An excess of sodium hydroxide. Has zinc hydroxide any acid properties? This is a chief difference between zinc and the other metals of this group.

(*b*) An excess of ammonia. (See Silver, 2.)

(*c*) (1) Hydrogen sulphide in *excess:* filter the solution and add ammonia and ammonium sulphide to the filtrate.
  (2) A few drops of hydrochloric acid and then hydrogen sulphide.
  (3) A few drops of acetic acid and some sodium acetate and then hydrogen sulphide in *excess* and proceed as in (1).

Consider the ionization equilibrium for hydrogen sulphide and explain briefly the difference in the results of (*c*) (1), (2) and (3).

3. The most sensitive test for zinc salts is afforded by its spectrum when a drop of a solution is tested with the aid of an electric spark. 0.001 milligram can be identified with certainty in a drop of its solution, the characteristic zinc lines flashing up occasionally.

Manganese; the Manganous Ion, $Mn^{\cdot\cdot}$.

1. What oxides does manganese form? (Read Smith or Remsen.) Which have base-forming properties, which acid-forming? How does the base- and acid-forming character change with the

increasing amount of oxygen in the oxides? From which oxide are the common salts, the chloride, sulphate, etc., derived? From which oxide are the permanganates derived?

(*a*) Fuse a minute quantity of any manganese compound with a little sodium carbonate and potassium chlorate. This affords a sensitive and characteristic test for manganese. Sodium manganate, Na_2MnO_4, is formed.

(*b*) Heat a very small amount of a manganese salt with lead dioxide or minium (they must be free from manganese; test the lead compound used by making a blank test) and nitric acid to boiling and allow the liquid to clarify. This reaction gives another sensitive test for manganese. The product is permanganic acid, $HMnO_4$.

2. Add to a manganese salt solution: (*a*) Sodium hydroxide in excess; (*b*) Ammonia in excess; (*c*) Acetic acid and hydrogen sulphide. Compare the results with those obtained with Zinc, 2.

Characteristics of the Fourth or Ferrous Group. — The hydroxides of the metals of the group are moderately strong bases. They form difficultly soluble sulphides and carbonates even in the presence of water, but the hydroxides are sufficiently soluble not to be precipitated by ammonia in the presence of ammonium chloride (differences from the aluminium group). The sulphides are precipitated by ammonium sulphide in neutral or alkaline solutions (difference from the aluminium alkaline earth and alkali groups), but are not precipitated by hydrogen sulphide in moderately acid solution (difference from the copper and arsenic groups).

Ask for an unknown mixture of salts of metals of the third and fourth groups.

ANALYSIS OF THE THIRD AND FOURTH OR IRON GROUPS.[1]

I. *Precipitation of the Iron Groups and Separation from the Alkalies and Alkaline Earths.*

1. First add some ammonium chloride to the solution, then ammonium hydroxide until the solution is just alkaline, irrespective of the formation of any precipitate, and finally add a

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[1] The aluminium and ferrous groups (III and IV) are often classified together as the "Iron Groups," ferric iron occurring in one group, ferrous iron in the other. The student should be sufficiently familiar with the members of all groups to recognize any one by the name of *any* representative.

small *excess* of ammonium sulphide. In this way $Al^{\cdots}$, $Cr^{\cdots}$, $Fe^{\cdots}$, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ni^{\cdot\cdot}$ $Co^{\cdot\cdot}$ are separated from $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, etc. Why is ammonium chloride used? When you have found by test that sufficient ammonium sulphide has been added, heat the mixture and stir it for a few minutes, then transfer the precipitate (**P**) to a filter and examine the filtrate as follows:

2. *Filtrate.* — If the filtrate is brown, a trace of *nickel* is indicated. To find it, boil the ammonia out of the solution under a hood, or make the solution faintly acid with acetic acid; the slight precipitate is collected upon a small filter paper, the paper incinerated and the ash tested with a minute borax bead.

3. *Precipitate* (**P**). — What substances may be present in this precipitate? Write the formulæ of all of the possible compounds. Put the precipitate in a beaker and treat it with an excess (usually 100 to 150 c.c.) of cold, very dilute, hydrochloric acid (one volume of dilute acid (sp. g. 1.12) to three volumes of water). Add this acid as long as there is effervescence of hydrogen sulphide. A black residue (**R**) may contain *nickel* and *cobalt* sulphides; the acid solution (**S**) may contain salts of the remaining metals of the iron groups, besides traces of nickel and cobalt.

II. -*Analysis of the Residue* (**R**) *insoluble in Dilute Hydrochloric Acid. Cobalt and Nickel.*

1. Test the residue with the borax bead. Either cobalt or nickel will be recognized or a mixture of both indicated.

2. If the test showed *cobalt,* test for *nickel* as follows:[1] Dissolve about half of the residue (*R*) in a *little* concentrated hydrochloric acid and a little nitric acid, evaporate the solution on a water-bath almost to dryness, dissolve the residue in water and a few drops of hydrochloric acid, then add sodium hydroxide to alkalinity and a very little acetic acid until the solution is again *slightly* acid to litmus paper. (X.)[2] Add to the solution a dilute solution of potassium cyanide (Poison! Care!) *drop by drop* until any *colored* precipitate which may form is just redissolved (not the colorless silica or alumina which sometimes appears); then add only two or three drops more of the potassium cyanide solution. If no heavy precipitate is formed by the first two or three *drops* of the cyanide, not more than three or four more *drops* are

[1] Read the whole method first.

[2] This is merely a sign for future reference.

added. Warm the solution gently. Add a large amount of sodium hydroxide solution and then an excess of bromine water. Let the bromine water float first on top of the liquid, to get a *local excess,* and observe whether a *black coloration* appears. If it does show, it may disappear when the liquid is shaken, but then a black precipitate will finally result, if *sufficient* bromine water and sodium hydroxide are used. Warm the solution, collect any black precipitate on a small filter, *wash it thoroughly* with hot water, and test the precipitate with the borax bead to confirm *nickel.*

N. B. — A large excess of potassium cyanide must be avoided because nickelic hydroxide cannot be precipitated until the excess is destroyed by the bromine. A few drops excess is all that is required to prevent the precipitation of cobalt. (In case of a negative result, consult the instructor before throwing away materials, etc.)

3. If the bead test of (**R**) (see II, § (1)) shows *nickel,* test for *cobalt* by the potassium nitrite method. Proceed with (**R**) as above in 2 to the point marked (X) (*do not add potassium cyanide*), then add more acetic acid and precipitate cobalt with a large excess of potassium nitrite, allowing the mixture to stand some time. Confirm *cobalt* in the precipitate, with the borax bead.

III. *Analysis of Solution* (**S**) *for Iron, Chromium, Aluminium; Manganese and Zinc* (*traces of Nickel and Cobalt*).

1. Boil the solution to remove hydrogen sulphide, add a *little* potassium chlorate or bromine water to the hot solution, until the odor of chlorine or bromine is perceived; then test a *small portion* of the solution for *iron,* by means of ammonium thiocyanate, or potassium ferrocyanide. Test the original unknown for *ferrous* (p. 18, 1) and *ferric iron* [p. 16, 4 (*a*) or 4 (*c*)].

2. Remove any chlorine or bromine present, by boiling the remainder of the solution obtained in 1, cool it and then neutralize it by adding sodium carbonate until a *permanent* precipitate is formed. Redissolve this precipitate in hydrochloric acid, which must be added only until the precipitate has *just disappeared.* To this *slightly* acid solution add an excess of the mixture of solid barium carbonate and water. Shake or stir the solution with the barium carbonate, and let the mixture stand until the supernatant liquid is colorless; then filter it. The precipitate (**P**) must

be tested for chromium and aluminium according to 3 (*a*) or 3 (*b*), the filtrate (F) for manganese and zinc and traces of nickel and cobalt according to IV.

3. (*a*) Test a part of the precipitate (P) for *chromium* by fusing some of it with sodium carbonate and potassium chlorate. Extract the fused mass with water; if it was green (*manganate*), boil the solution with a single drop of alcohol and filter it again. In either case, if the filtrate is yellow (compare the color of the solution with that of pure water), chromic acid is present; the addition of acetic acid and lead acetate will give yellow lead *chromate*.

Test the precipitate (P) for *aluminium* by boiling a considerable portion of it with water, to which a gram or two of solid barium hydroxide and an equal amount of sodium carbonate have been added; filter, acidify, and boil the solution, and add ammonium hydroxide in *small* excess. (Litmus.) A flocculent precipitate shows the presence of *aluminium*. (Write out the reaction equations which show the changes of aluminium from the very beginning of the analysis.)

(*b*) Treat a part of the precipitate (P) with a *small* amount of sodium peroxide (Care!). A yellow solution of sodium chromate proves the presence of *chromium*. The solution is acidified with hydrochloric acid and ammonia added to slight alkalinity, and the mixture boiled. A white precipitate is *aluminium* hydroxide.

IV. *Analysis of Filtrate* (F) *for Manganese and Zinc* (*and Traces of Nickel and Cobalt*).

1. Heat the filtrate (F) to boiling and add sulphuric acid to remove barium. Filter the solution, concentrate it and precipitate *manganese* and *zinc* by means of ammonium hydroxide and ammonium sulphide, heating the mixture two or three minutes. Bring the precipitated sulphides on a filter, and treat them with an excess of dilute hydrochloric acid (one part dilute acid to three parts of water).

2. A small black residue remaining undissolved would be nickel or cobalt sulphide, dissolved by the acid in I. If they have been found in II, this residue need not be tested; otherwise it is examined according to II for nickel and cobalt.

3. (*a*) Filter the solution, boil it to expel hydrogen sulphide. Then add sodium hydroxide in excess. If a precipitate forms

collect it upon a filter-paper, and test it for *manganese* by fusing some of it with sodium carbonate and potassium chlorate. If the precipitate is small, incinerate the filter-paper and test the ash. (Write out an account of the changes which manganese goes through from the beginning of the analysis.)

(*b*) The alkaline solution which has been separated from the manganese is tested for *zinc* by adding hydrogen sulphide water or a drop of ammonium sulphide to it.

THE FIFTH OR THE SILVER-COPPER GROUP

Silver, Lead, Mercurous and Mercuric Mercury, Bismuth, Copper and Cadmium.

(*Complex Ions and their Instability Constants.*)

Group Reactions. — 1. (*a*) Pass hydrogen sulphide into dilute solutions of silver, lead, mercurous, mercuric, copper, cadmium and bismuth nitrates, to each of which a few *drops* of dilute nitric acid have previously been added. Note the colors of the precipitated sulphides. Compare the behavior of these salts with those of the metals of the zinc group [p. 18, 4 (*c*)].

What is the action of a strong acid on the condition of equilibrium of hydrogen sulphide and its ions? To what is the difference in behavior of the salts of the two groups ultimately due? Is a physical or a chemical difference the cause of the different behavior? (Lecture.)

(*b*) Add to a few c.c. of cadmium nitrate or sulphate solution 4 or 5 c.c. concentrated hydrochloric acid and pass hydrogen sulphide into the solution as long as it is absorbed. Then dilute the mixture with four or five volumes of water, and pass more hydrogen sulphide into the solution. Explain the results on the basis of the conditions of chemical and physical equilibrium obtaining. Lead salts behave in the same way.

(*c*) Repeat (*b*) with copper sulphate. Explain the difference in the results of (*b*) and (*c*). (Lecture.)

Under what conditions must we use hydrogen sulphide to get a complete precipitation of this group?

2. Precipitate bismuth sulphide as in 1 (*a*), filter and wash the precipitate and digest it then with several c.c. ammonium sulphide. Does it dissolve perceptibly? Filter the liquid from the precipitate

and add dilute hydrochloric acid to the filtrate. Is any bismuth sulphide reprecipitated?

The behavior of bismuth sulphide is typical for all the sulphides of the group and distinguishes them from the sulphides of the metals of the sixth or arsenic group.

NOTE.—*Copper* sulphide is very sparingly soluble in ammonium sulphide.

Silver Ion, $Ag^{\cdot}$.

1. (*a*) Test silver nitrate solution with neutral litmus. Is it the salt of a weak or a strong base?

(*b*) Add sodium hydroxide in excess to silver nitrate. Has the silver oxide (silver hydroxide) any tendency to form a sodium salt or any acid properties?

(*c*) Add ammonia drop by drop in excess to silver nitrate solution. The silver oxide dissolves readily in excess of ammonia. Can this be due to any acid properties of silver hydroxide and the formation of an "ammonium argentate"? Which would form a salt more readily with a weak acid, sodium hydroxide or ammonium hydroxide? Justify your conclusion either by the laws of equilibrium or by recalling experimental facts bearing on the question.

2. The ammonia forms a complex positive ion with silver (Lecture), according to the following equation:

$$\overset{+}{Ag} + 2NH_3 \rightleftarrows (Ag,\overset{+}{2}NH_3).$$

Apply the law of mass action or chemical equilibrium to this system and express mathematically what would be constant in the system. If we put the concentration of the complex ion in the denominator, the constant has a value $k = \frac{1}{10^7}$, and is called the "*instability constant*" of the complex ion.[1] According to this value, can there be many silver ions in an ammoniacal silver solution? Might it be possible to precipitate *any* silver salts, at all, from such a solution? (Test your conclusion, below, according to (*a*).) Will silver salts be precipitated as easily from such an ammoniacal solution as from a silver nitrate solution? (See (*b*).) What effect will a considerable *excess* of *ammonia* have on the

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[1] Bodlaender, Zeitschrift für physikalische Chemie, **39**, 597 (1902) and Berichte der deutschen chemischen Gesellschaft, **36**, 3933 (1903).

silver ions according to the above equation? Will it facilitate the precipitation of silver salts? (See (*c*).)

(*a*) Add sodium hydroxide to a few c.c. of silver nitrate, then fill the test-tube with water, let the silver oxide subside and decant the liquid. Wash the precipitate twice in the same way, then dissolve it in ammonia added drop by drop until the precipitate has just redissolved, and then to have a small excess of ammonia add one or two drops excess of ammonia, *not more*. To one-third of the solution add sodium chloride.

(*b*) Add a few drops of sodium chloride and sodium phosphate to separate portions of silver nitrate. Then add sodium phosphate to a second third of the ammoniacal silver solution prepared in (*a*). Why should silver chloride have been precipitated in the ammoniacal solution and silver phosphate not? Devise a simple experiment to test your conclusion. (Lecture.)

(*c*) To the last third of the ammoniacal silver solution obtained in (*a*) add a larger excess (2 or 3 c.c.) ammonia, and then add sodium chloride. Explain the difference between (*a*) and (*c*). Is the silver ion completely suppressed? Add a drop of ammonium sulphide to part of the ammoniacal silver solution, and then answer the question.

(*d*) To the solution (*c*), in which sodium chloride failed to give a precipitate, add, after the sodium chloride, nitric acid. Explain the effect of the nitric acid on the basis of the equilibrium equation established above. *Silver* is identified by the solution of its chloride in ammonia and its reprecipitation by acidifying the solution.

3. Precipitate some silver chloride, bring it on a filter and expose some of it to sunlight. Mix another small portion with sodium carbonate and heat the mixture on charcoal with a blowpipe. Cut out the contents of the cavity, treat the mass with water in a mortar, throw away the floating particles of charcoal and rub the heavier particles in the mortar vigorously with a pestle.

Lead Ion, $Pb^{\cdot\cdot}$.

1. Repeat with lead nitrate 1 (*a*), (*b*), (*c*) described under "Silver." Has lead hydroxide any acid properties? Does it resemble silver in its behavior toward ammonia?

2. To 10 c.c. of a solution of lead nitrate add hydrochloric

acid. Bring the precipitated chloride on a filter and wash it with some water.

(*a*) Treat about half of the lead chloride with about 50 c.c. boiling water. It is quite soluble in hot water, differing in this respect from silver and mercurous chlorides. Cool the solution, filter from the separated crystals and use the filtrates for (*b*), (*c*) and (*d*).

(*b*) Add hydrogen sulphide to a part of the filtrate. Is lead chloride at all soluble in *cold* water? Add to another portion sulphuric acid. Is the sulphate less soluble than the chloride?

(*c*) Add to a further portion of the cold solution of lead chloride potassium chromate. Let the precipitate subside, decant the liquid and add sodium hydroxide to the precipitate. Why does the precipitate dissolve? (See 1 (*b*).) Add acetic acid to the alkaline solution. The lead chromate will be reprecipitated. *Lead* is best identified as the chromate by this series of reactions. Give their equations.

(*d*) Add to a further portion of the saturated lead chloride solution obtained in (*a*) a little of a concentrated solution of sodium chloride. The precipitate is lead chloride. Explain how it is formed.

3. Mix a portion of the solid lead chloride obtained in 2 with some sodium carbonate and reduce it to lead with the aid of the blow-pipe.

Mercury; Mercurous Ion, $Hg^{\cdot}$.

1. Add to mercurous nitrate: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess; (*c*) hydrochloric acid. What is the familiar name of the last precipitate? Decant the liquid, wash the precipitate once with water by decantation and then treat a portion with hot water, another portion with ammonia. (Difference from lead and silver chlorides.) *Mercurous mercury* is identified by this action towards ammonia.

2. Mix a little dry mercurous or mercuric salt with sodium carbonate in a narrow glass-tube, three inches long and closed at one end. Cover the mixture with a little pure dry sodium carbonate in the tube, leaving two inches free, and heat the contents, advancing from the pure carbonate to the mixture.

Mercury ; Mercuric Ion, $\mathrm{Hg}^{\cdot\cdot}$.

1. Add to mercuric nitrate: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess; (*c*) hydrochloric acid.

2. Treat mercuric chloride solution with stannous chloride in excess. Mercurous chloride and then mercury are precipitated. *Mercuric mercury* is identified by this action. Give the equations of the reactions. What is the familiar name for mercuric chloride?

3. See, above, the behavior of mercuric salts when heated with sodium carbonate (p. 28, 2).

Copper ; Cupric Ion, $\mathrm{Cu}^{\cdot\cdot}$.

1. Add to a solution of copper sulphate: (*a*) sodium hydroxide in excess; (*b*) ammonia in excess. Is a complex ion formed with the ammonia? (*c*) Potassium cyanide (Care!), added drop by drop, until the precipitate has redissolved, and then a few drops excess. Copper forms with potassium cyanide complex negative ions, as do cobalt, nickel, ferrous and ferric iron, silver and other metals. We have, for instance:

$$2\,\overset{+}{\mathrm{K}} + \overset{++}{\mathrm{Cu}} + 4\,\mathrm{C\overline{N}} \rightleftarrows (\mathrm{Cu}(\mathrm{C\overline{N}})\overline{{}_4}) + 2\,\overset{+}{\mathrm{K}}$$

or

$$\overset{++}{\mathrm{Cu}} + 4\,\mathrm{C\overline{N}} \rightleftarrows (\mathrm{Cu}(\overline{\mathrm{C}}\overline{\mathrm{N}})_4).$$

Give the mathematical equilibrium equation for the last equation. The constant of the equation is called the *instability constant of the complex ion.* Judge from the following experiments (1–3) which is more stable, the complex ion of copper with ammonia or the complex ion of copper with cyanogen:

(1) Add a considerable excess of ammonia to some copper sulphate. To a portion add ammonium sulphide.
(2) To a portion of the cyanide solution obtained in (*c*) add ammonium sulphide.
(3) To some of the blue solution (1) add a few crystals of potassium cyanide, until the blue color is discharged.

(*d*) Add to cadmium sulphate a small excess of potassium cyanide. Add hydrogen sulphide. (Difference from copper.) Recall the result of 1 (*b*) and (*c*) of the Group Reactions of the "Silver-Copper" group, (p. 25), and then decide whether the complex ion of copper with cyanogen or that of cadmium is the *more stable.*

(*e*) Recall 5 (*a*) under ferric iron and 4 (*b*) under nickel and cobalt. What could you say of the stability constant of the ferricyanide ion $(\bar{\mathrm{Fe}}(\overline{\mathrm{CN}})_6)$? of the nickel cyanide ion $(\mathrm{Ni(CN)_4})$? Explain now the effect of conc. hydrochloric acid on ferricyanides (5 (*a*), p. 16) using the equilibrium equation for the complex ion and the fact that hydrocyanic acid is an extremely weak acid. (Lecture.)

2. (*a*) Add to copper sulphate some potassium ferrocyanide. This is a sensitive *copper* test in the wet way.

(*b*) Heat a copper salt with sodium carbonate in the reducing flame before the blow-pipe. Treat the mass according to p. 27, 3.

(*c*) Heat a little copper salt with a borax bead in the oxidizing flame, and then in the reducing flame, after adding a very little stannous chloride.

(*d*) Heat some copper chloride on the end of a copper wire in the Bunsen flame.

Cadmium Ion, $\mathrm{Cd}^{\cdot\cdot}$.

1. Add to cadmium nitrate: (*a*) an excess of sodium hydroxide; (*b*) an excess of ammonia; (*c*) hydrogen sulphide.

2. Recall 1 (*b*) of the "Silver-Copper" group and 1 (*d*) under Copper.

3. Heat some cadmium salt with sodium carbonate in the reducing flame of the blow-pipe. Note the brown coating of cadmium oxide surrounding the cavity in the charcoal. What does the presence of this coating show as to the volatility of metallic cadmium?

4. *Cadmium* is usually identified by means of its *yellow sulphide* which is insoluble in ammonium sulphide (difference from arsenic and stannic sulphides). We can detect and identify it with greatest certainty by means of the spectroscope, the electric spark being used with a drop of a solution (see under Magnesium). As little as 0.0001 milligram can be identified in a drop of liquid.

Bismuth Ion, $\mathrm{Bi}^{\cdot\cdot\cdot}$.

1. Test a solution of bismuth nitrate with litmus. What would you say as to the strength of bismuth hydroxide as a base?

2. Add to bismuth nitrate:

(*a*) Sodium hydroxide in excess.

(*b*) Ammonia in excess. Use the precipitate for 3.

3. Bring the precipitated bismuth hydroxide on a filter, dissolve it in hydrochloric acid, and add water to the solution. The precipitate is bismuth oxychloride, a basic bismuth chloride, formed according to

$$BiCl_3 + H_2O \rightleftarrows \underline{(BiO)Cl} + 2\,HCl.$$

Under what conditions will the test be most sensitive, in the presence of much or little hydrochloric acid, much or little water? Properly applied this is one of the best tests for bismuth.

4. Add to a little stannous chloride an excess of sodium hydroxide and to the solution of sodium stannite thus formed add a few drops of a solution of a bismuth salt. The brown precipitate is bismuthous oxide. This is another very sensitive test for bismuth.

5. Bismuth gives also a characteristic spark spectrum.

6. Reduce some bismuth salt before the blow-pipe. The globules of the metal are quite brittle.

Characteristic Properties of the Silver-Copper Group.

The *hydroxides* of the metals of this group are pronounced bases; only lead hydroxide is amphoteric, but its basic character predominates.

The *sulphides* of the metals of this group are more insoluble in water than those of the previous groups, and are precipitated by hydrogen sulphide even from solutions containing a moderate excess of a strong acid (difference from all the previous groups).

The *sulphides* have no acid-forming properties and are insoluble in ammonium sulphide (difference from the Arsenic Group). All the sulphides excepting the sulphide of mercury dissolve in hot nitric acid.

Three of the ions of the group, silver, mercurous mercury and lead, form difficultly soluble *chlorides*, and advantage is taken of that fact to separate them from the other ions of the group.

ANALYSIS OF THE SILVER-COPPER GROUP.

Add to the aqueous or nitric acid solution dilute hydrochloric acid, drop by drop, as long as a precipitate forms, and then an excess of ten or twelve drops to redissolve any bismuth oxychloride. Bring the precipitated chlorides (P) on a filter and wash them with a little water. Reserve the filtrate (F) for further analysis.

Analysis of the Precipitate (Silver Division).

1. Pour 3 or 4 c.c. hot water over the precipitate (P) on the filter, and test the liquid running through the filter for lead according to 2 (*c*) under Lead. If *lead* is found, extract the lead chloride with hot water, until sulphuric acid (2 (*b*), p. 28) shows the washings are free from lead.

2. Treat the residue on the filter with ammonia: a black precipitate remaining on the filter is proof of the presence of *mercurous* mercury. It can be washed with water, treated with hydrochloric acid and a small crystal of potassium chlorate, the solution diluted and filtered and treated with stannous chloride: a white or gray precipitate confirms *mercury*.

3. The ammoniacal filtrate is acidified with nitric acid, used in small *excess*. A precipitate shows the presence of *silver*.

NOTE: *Lead* chloride is sparingly soluble in water and it cannot be completely precipitated, and small quantities of lead would not be precipitated at all as chloride, but would be found only in the filtrate F().

Analysis of the Filtrate (Copper Division).

Into the filtrate (F) pass hydrogen sulphide *in excess* (Test?). Would the first precipitate formed contain some of each of the sulphides or would they come down one after the other in chief part? Bring the sulphides on a filter, dilute a portion of the filtrate with three or four volumes of water and pass more hydrogen sulphide into the diluted solution (*vide* 1 (*b*), Silver-Copper Group, p. 25). If a precipitate is formed, treat the whole filtrate in the same way and add the sulphide to the rest of the sulphides on the filter.

4. The precipitated sulphides are washed twice with water to remove hydrochloric acid and then brought into a porcelain dish and boiled two or three minutes with about ten volumes *dilute* nitric acid. The solution (S) is cooled, diluted and filtered from the residue, and reserved for 6. The residue may contain sulphur, *mercuric* sulphide (black), *mercuric* sulphide-nitrate (white), lead sulphate and small amounts of *cadmium*.

5. Treat a portion of this residue with hot dilute hydrochloric and a few crystals of potassium chlorate. The solution is cooled,

diluted and a portion tested for *mercury* with stannous chloride. The rest of the solution is evaporated to dryness in a porcelain dish under a good hood and the residue gently heated to remove the mercuric chloride. (Care! The mercuric chloride or *corrosive sublimate* vapor is a *poison;* the operation must be carried out under a *good hood with the gas lit* in the flue and the hood closed!) The residue in the cooled dish is dissolved in a little water and a drop of hydrochloric acid, the solution filtered and tested for *cadmium* with hydrogen sulphide.

6. To the solution (**S**) a little sulphuric acid is added in order to test it for *lead,* if it has not been found before; to *remove it,* if it has been found. Evaporate the solution in a porcelain dish with the sulphuric acid over a small flame until fumes begin to come off, *cool* the residue and treat it with water and a little dilute sulphuric acid and filter the solution at once from any white precipitate (*lead* sulphate) that may be left. If *lead* has not been identified before, the lead sulphate is covered with potassium chromate solution, the mixture warmed — the less soluble lead chromate is thereby formed; a moderate excess of sodium hydroxide is added to the mixture, the liquid is filtered and acidified with acetic acid. A yellow precipitate would be *lead* chromate. (See Lead, 2 (*c*) p. 28.)

7. The filtrate from the lead sulphate is still to be tested for *bismuth, cadmium* and *copper.* An excess of ammonia is added to it. A precipitate is collected and tested for *bismuth* according to Bismuth, 3 or 4. Unless one of these tests is obtained the presence of bismuth has not been demonstrated.

8. If the ammoniacal solution is blue, *copper* is present. If it is not blue, part of it is tested for a trace of *copper* by means of acetic acid and potassium ferrocyanide (p. 30). Even a faint pink tint indicates *copper.*[1]

9. In the presence of copper, we test for *cadmium* by adding potassium cyanide to the blue ammoniacal solution until the color is discharged; a few drops excess of cyanide and then hydrogen sulphide are added. A yellow or yellowish precipitate would show the presence of *cadmium.* In the absence of copper, the treatment with potassium cyanide is omitted. Frequently the

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[1] Cadmium ferrocyanide is white and its color reduces the intensity of color of the copper salt.

cadmium sulphide is discolored by traces of a black sulphide. If the color of the precipitate makes the presence of cadmium doubtful, the precipitate may either be warmed with hydrochloric acid and tested with the spectroscope (Cadmium 4), or it is boiled with three or four c.c. dilute sulphuric acid, the solution is filtered, diluted, made neutral with ammonia and acidified with a *drop* or two of acid only (why?) and treated with hydrogen sulphide to reprecipitate any *cadmium* sulphide.

THE SIXTH OR ARSENIC GROUP

Arsenic, Antimony, Tin, Gold and Platinum.

Group Reactions. — 1. (*a*) Cover some arsenious oxide with water and add sodium hydroxide to the mixture and warm it. What is formed?

(*b*) Add an excess of hydrochloric acid to a mixture of arsenious oxide and water, and warm the mixture. What is formed? According to (*a*) and (*b*) arsenious hydroxide is both acid and base. *Its acid properties are more pronounced* and it is called arsenious *acid.* This is the characteristic feature of the arsenic group, *especially in the case of the higher oxides* (each metal forms two oxides, As_2O_3, As_2O_5; Sb_2O_3, Sb_2O_5; SnO, SnO_2; Au_2O, Au_2O_3; PtO, PtO_2). As far as the higher oxides are concerned we are dealing essentially with a *group of acid-forming oxides,* with subordinate base-forming properties. *This is the chief difference between the arsenic group and all the previous groups.*

2. (*a*) Dissolve some sodium stannate in water, add hydrochloric acid until the precipitated stannic acid is redissolved as the chloride, and pass hydrogen sulphide into the solution. Bring the sulphide on a filter and wash it. Treat some of it with a solution of ammonium sulphide. What is formed? (Lecture.) Compare the result with that obtained in 1(*a*).

(*b*) Treat a solution of sodium sulpho-stannate with an excess of hydrochloric acid. Note the gas that is given off. What is the precipitate? What unstable acid is first liberated? What unstable oxygen acid do you know of that behaves in a similar manner? Arsenic, antimonic, auric, and platinic sulphides show the same behavior as stannic sulphide shows in (*a*) and (*b*), and *this behavior is characteristic of the group and is used to separate the*

group from the sulphides of the metals of the previous group. Is the difference a chemical or a physical one?

3. (*a*) Add an excess of sodium hydroxide to a solution of stannous chloride. Has stannous hydroxide any acid properties? Has it any basic properties?

(*b*) Add ammonia in excess to a solution of stannous chloride. Explain the difference in the result of (*a*) and (*b*). Can stannous hydroxide be a strong acid?

(*c*) Pass hydrogen sulphide into a solution of stannous chloride. Bring the precipitate on a filter (note its color), and treat part of it with colorless ammonium sulphide. In contrast to stannic sulphide (2 (*a*)), the precipitate hardly dissolves (compare the result with the behavior of the hydroxide in 3(*b*)). Add to the mixture some pulverized roll sulphur, and warm the mixture. Add an excess of hydrochloric acid to the solution obtained. What is the yellow precipitate? Explain the action of the sulphur.

As a rule the sulphur is dissolved in the ammonium sulphide before the latter is used, and so-called "yellow" ammonium sulphide containing persulphides $(NH_4)_2S_x$ is used ready prepared. This dissolves the lower sulphides as well as the higher sulphides of the group, sulphurizing the lower ones. Which are the *stronger acid-forming* sulphides and oxides, the lower or the higher ones in the group?

Arsenic Ions, $As^{\cdot\cdot\cdot}$ *and* $As^{\cdot\cdot\cdot\cdot\cdot}$; $\bar{A}\bar{s}\bar{O}_3$ *and* $\bar{A}\bar{s}\bar{O}_4$.

1. See 1 under *Group Reactions* (p. 34) in regard to the behavior of arsenious acid.

Pass hydrogen sulphide into the hydrochloric acid solution of some arsenious acid. Note the color of the precipitate and note whether the latter forms *at once*. Give the equations.

2. (*a*) Add a small excess of dilute hydrochloric acid to a solution of potassium arseniate to prepare a solution of arsenic acid, (H_3AsO_4), and pass hydrogen sulphide into the *cold* solution. Compare the result with 1. Now heat the solution and continue the treatment of the hot solution with hydrogen sulphide for some time. Collect the precipitate on a filter, wash it and then treat it with ammonia. What is left on the filter? Acidify the filtrate with hydrochloric acid. What is the action of hydrogen

sulphide on arsenic acid under these conditions? (Lecture.) Give the equations.

(*b*) Add to a solution of potassium arseniate concentrated hydrochloric acid to an acid reaction and then add a further excess of two volumes of the concentrated acid and pass hydrogen sulphide into this solution in the cold. After some time, dilute the mixture somewhat and collect the precipitate. Treat it with an excess of ammonia. It should all dissolve. What is the action of hydrogen sulphide on arsenic acid under these conditions? Give the equations. What do the experiments (*a*) and (*b*) show in regard to faint basic properties of arsenic acid and the formation of a quinquivalent arsenic ion in (*b*)? [1] (Lecture.)

The difficulty in precipitating arsenic sulphide in the cold under the conditions (*a*) used *for all other sulphides* of this and the previous group is characteristic for arsenic acid (H_3AsO_4) and is due to its being the most *pronounced acid* and the least basic of all the hydroxides. *This fact must be always borne in mind in testing for arsenic, as even large quantities of the poisonous element may otherwise be overlooked.*

3. Add to potassium arsenite and arseniate solutions:

(*a*) Silver nitrate. Note the colors of the salts. They distinguish arsenites from arsenates.

(*b*) Ammonium chloride, magnesium chloride and ammonium hydroxide.

(*c*) Nitric acid to acidify the solutions and five or six volumes of "ammonium molybdate" solution and heat the mixtures to boiling. The arseno-molybdate precipitate is a characteristic test for *arsenic* in the arsenic acid form.

4. (*a*) Prepare a glass tube four inches long and drawn out to a narrow, sealed point at one end. Place a very *little* arsenious oxide in the narrow point and a piece of charcoal in front of it; heat the charcoal first to redness and let the heat spread very slowly towards the oxide, but keep the front half of the tube cold. What is the silver-gray sublimate that is formed? Explain the reaction, and give its equation.

(*b*) Prepare a similar tube, but blown out to a small bulb at one end. Mix a little arsenic sulphide, dry sodium *carbonate* and dry potassium cyanide (Care!) in a mortar and heat a little

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[1] *Vide*, Neher, Zeitschr. für Anal. Chemie, **32**, 45 (1893).

of the mixture in the bulb of the tube. What is the sublimate? (Difference from antimony.) For what purpose is the potassium cyanide used? Give the equation.

(*c*) Heat a *very* small amount of arsenious oxide, mixed with sodium carbonate, in the reducing flame of the blow-pipe on charcoal and note the garlic-like odor of the arsenic. (Poison!)

(*d*) Read Fresenius, p. 284, on the Marsh test for arsenic. Students may make the test under the guidance of the assistant or may leave it to an advanced course.

(*a*), (*b*), (*c*) or (*d*) may be used as sensitive characteristic tests for arsenic, the Marsh test being the best but longest.

Antimony Ions, $Sb^{\cdot\cdot\cdot}$ *and* $Sb^{\cdot\cdot\cdot\cdot\cdot}$.

1. What is the color of the sulphides of antimony? It is used as characteristic of antimony. Treat some sulphide with warm concentrated hydrochloric acid (difference from arsenic).

2. Add antimonous chloride to a large excess of water. Recall what other metal chloride shows a similar behavior. Let the precipitate subside, decant the liquid, and add a solution of tartaric acid to the precipitate. (Read Smith or Remsen.)

3. (*a*) Add to a solution of antimonous chloride a steel nail and enough hydrochloric acid to produce a good evolution of hydrogen. The black precipitate produced is a characteristic test for antimony.

(*b*) Place a small piece of tin on a piece of platinum foil in a porcelain dish, add a little hydrochloric acid and a drop of the solution of antimony chloride. A black precipitate is produced on the platinum. It may be washed with water and treated with a solution of sodium hypobromite without dissolving.

(*c*) Reduce some antimonous oxide before the blow-pipe.

Tin Ions, $Sn^{\cdot\cdot}$ *and* $Sn^{\cdot\cdot\cdot\cdot}$.

1. (*a*) Treat a solution of sodium stannate with a small excess of hydrochloric acid and pass hydrogen sulphide into the solution obtained. Bring the precipitate on a filter and treat a part with warm concentrated hydrochloric acid. (Difference from arsenic sulphides.)

(*b*) See § 3 in the "group reactions," p. 34.

2. Add stannous chloride solution to a solution of mercuric chloride. Add a steel nail to a solution of stannic chloride; after a few minutes, decant the solution, dilute it and add to it some mercuric chloride. This is a characteristic test for tin. Explain the reactions.

Platinum Ions, $Pt^{\cdot\cdot}$ *and* $Pt^{\cdot\cdot\cdot\cdot}$*, and Gold Ions,* $Au^{\cdot}$ *and* $Au^{\cdot\cdot\cdot}$.

Note: Put all platinum and gold residues into the appropriate bottles on the side-shelf.

1. (*a*) Add a drop of chloroplatinic acid, H_2PtCl_6, to potassium chloride. What is the composition of the precipitate? From what ions was it formed? Read Remsen, pp. 465, 614, 729, on chloro-acids, chlorauric and chloroplatinic acids.

(*b*) Add a drop of silver nitrate to a drop of chloroplatinic acid; then add a few drops of ammonia. Is the precipitate silver chloroplatinate or silver chloride?

(*c*) Pass hydrogen sulphide into a drop or two of chloroplatinic acid diluted with a little water. Does a sulphide form readily? Heat the mixture. Does chloroplatinic acid give any positive ions of platinum at all? On the basis of (*a*), (*b*), (*c*), give a complete statement of the ionization of chloroplatinic acid, and indicate the chief ions formed. Can $\overline{Pt}\,\overline{Cl}_6$ be considered a complex ion?

2. Treat the sulphide obtained in 1 (*c*) with a few drops of ammonia and ammonia sulphide. It will ultimately dissolve to give ammonium sulphoplatinate (see p. 34, 2). What are its ions? Can $\overline{Pt}\,\overline{S}_3$ be considered a complex ion?

(*d*) Read in Remsen on the platinates, p. 730, and the cyanogen platinous salts (e.g., $K_2Pt(CN)_4$). What four classes of *negative* ions does platinum enter into? Can they all be considered to be complex ions? Are there then complex ions of elements with oxygen? Is there any essential difference between the four classes?

2. (*a*) Treat two or three drops of gold chloride solution (Store-room) with a drop of hydrochloric acid and hydrogen sulphide; add a drop of ammonia and yellow ammonium sulphide to the precipitate.

(*b*) Repeat (*a*), but treat the sulphide with a few drops of potassium cyanide solution. Why does the cyanide dissolve the gold

sulphide? Electrolyze this solution for a few moments in a little cell and note *on which pole* gold is deposited (Instructor). Is this result consistent with the solubility of gold sulphide in the cyanide?

3. (*a*) Evaporate a drop each of the solutions of chloroplatinic acid and gold chloride on porcelain lids and ignite the residues gently. Give the equations for the reactions. Add to the metallic stains a drop of concentrated nitric acid. Then add to this a drop of concentrated hydrochloric acid, to produce aqua regia.

(*b*) Ignite a little precipitated silver chloride in like fashion on a porcelain lid. Is metallic silver formed? What do (*a*) and (*b*) show as to the relative stability of the metal chlorides?

4. (*a*) Mix some potassium chloroplatinate (from 1 (*a*)) with a little dry sodium carbonate and ignite the mixture in the loop of a platinum wire in the blow-pipe flame. Treat the mass then in an *agate* mortar (Store-room) with a little water and polish the platinum powder. Why is the platinum obtained as a powder?

(*b*) Ignite a little gold sulphide with or without sodium carbonate in the cavity of a piece of charcoal before the blow-pipe. Polish the gold in an ordinary mortar and note what minute quantities can be seen in this way.

5. Treat a drop of chloroplatinic acid and gold chloride each separately with water and

(*a*) Ferrous sulphate and a drop of hydrochloric acid.

(*b*) Oxalic acid.

(*c*) Potassium iodide.

6. Treat a drop of gold chloride in 10 c.c. water, drop by drop, with a stannous chloride solution prepared from a drop of the reagent in 10 c.c. water. The resulting color is the color of colloidal gold and is called Cassius purple.

Platinum and gold may be separated from the other metals of the arsenic group on the basis of the reactions studied under 3, or by other reduction methods, and distinguished from each other by 4 and 5. (See also pp. 69, 70, §§ 3 and 5).

Characteristics of the Arsenic Group. — The higher oxides and sulphides of the metals are pronounced acid-forming compounds. The sulphides combine readily with sodium and ammonium sulphides to form soluble alkali salts of sulpho acids (difference from all the previous groups). The sulphides are so insoluble that they are precipitated by hydrogen sulphide even in the presence of a small amount of a strong acid (difference from the iron, alkaline earth and alkali groups).

Gold and platinum, the so-called "noble metals," differ from the other metals of the group by their small affinity for oxygen and chlorine, in consequence of which their compounds are readily reduced and the metals formed. Advantage may be taken of this property in separating them from the remaining metals of this and the other groups.

ANALYSIS OF THE ARSENIC GROUP.[1]

A. 1. Pass hydrogen sulphide into the cold acid solution to saturation, filter the solution from the precipitate and then pass hydrogen sulphide into the heated solution to insure the precipitation of arsenic. (See above; which form of arsenic is precipitated with difficulty as the sulphide, the arsenious or the arsenic?) Collect any precipitate thus formed and test finally the *diluted* cold filtrate with hydrogen sulphide to see if any sulphide was kept from precipitation by too large an excess of acid. The combined sulphides are collected, drained on a filter-pump, transferred to a beaker and warmed with 3 to 5 c.c. conc. hydrochloric acid, as long as there is a *brisk* evolution of hydrogen sulphide. Antimony and tin sulphides dissolve (solution (S)); arsenious sulphide remains practically completely undissolved with sulphur, which is always present. The solution (S) is diluted with an equal volume of water and separated from the residue (R). This residue should be tested for *arsenic* in two ways. First, a small portion is boiled with 5 c.c. concentrated nitric acid as long as brown fumes form, to convert any arsenic into arsenic acid; part of this solution is diluted and heated to boiling with four or five volumes of molybdate solution (see Arsenic, 3 (*c*)). A second small portion of the arsenious sulphide is dissolved in a little ammonia, the solution is filtered and evaporated to dryness in a porcelain dish over a very small flame, after the addition of a little sodium carbonate. The dried residue is tested with potassium cyanide (Care!) in a tube according to p. 36, 4 (*b*).

2. The solution (S) is boiled to remove every trace of hydrogen sulphide and half of it is then treated with a steel nail or

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[1] Platinum and gold are not included here, but are included on p. 69.

two. A precipitate of black flakes indicates *antimony*; the *tin* remains in solution as stannous chloride, and, after diluting the solution, is identified by means of mercuric chloride. As steel gives a little carbon, which may be mistaken for *antimony*, the latter is best fully identified by converting it into the orange sulphide. The black precipitate is collected and warmed with some tartaric acid and a drop or two dilute nitric acid; the solution is diluted and saturated with hydrogen sulphide. Or a small portion of the solution (S) is tested for *antimony* according to antimony 3 (*b*) with platinum and tin.

B. Test a few *drops* of the original unknown for arsenic as follows: (Hofmann's modification of Marsh's test.) (*Use the hoods.*) Fit a 250-c.c. flask with a thistle (safety) tube and delivery tube, connect the latter with a U-tube half filled with glass beads (store-room) and the exit of the U-tube with a bent-glass tube dipping into a long test-tube. Moisten the glass beads with lead acetate, generate hydrogen in the flask from pure zinc and dilute hydrochloric acid and test whether all connections are air-tight by closing the exit a moment and observing whether the acid rises high in the thistle-tube. If the connections are good, bring 10 c.c. silver nitrate into the long test-tube, and bring *one drop* of the unknown solution into the thistle-tube, rinse it into the generator and let the gases pass through the silver nitrate for several minutes. (They are poisonous gases! Care!) A second and third drop may be used, if it seems necessary. Disconnect the generator and stop the evolution of any arsine by pouring the acid off the zinc (hood-sink) and rinsing it with water. Filter the silver nitrate solution from any precipitate formed (this may contain antimony, see Fresenius, p. 299), and cover the filtrate in a test-tube with a *zone* of diluted ammonia. At the neutral junction between the acid and alkaline zones, yellow silver arsenite will show if *arsenic* is present.

By a study of the "group characteristics," work out a scheme for separating the groups from each other. Show your method to an instructor and ask for an unknown containing a representative of each group.

B. REACTIONS OF THE ACID IONS.

Group Reactions.

1. Add silver nitrate and then nitric acid to: (*a*) sodium chloride; (*b*) sodium phosphate. Silver bromide, iodide, cyanide, sulphide, sulpho-, ferro-, and ferricyanide are, like the chloride, almost insoluble in cold, dilute nitric acid. We may call this the *hydrochloric acid group of acids.*

Silver (oxide), arsenite, arsenate, chromate, carbonate, silicate, borate, like the phosphate, are rather difficultly soluble in water, but readily soluble in nitric acid. We may call this the *phosphate group.* The silver salts of certain organic acids, as oxalic and tartaric acids, behave like silver phosphate.

Silver nitrate, chlorate, fluoride, sulphate, (acetate), are easily to moderately soluble in water. We may call this the *nitrate group.*

2. Mix four or five drops of sodium chloride solution with the same amount of the solution of tri-sodium phosphate, add a few c.c. water and then silver nitrate drop by drop, as long as a precipitate forms, shaking the mixture vigorously. Which silver salt is the less soluble in water? How does this account for the difference found in 1?

Hydrochloric, Hydrobromic and Hydroiodic Acids, HCl, HBr, HI; *Chloride, Bromide and Iodide Ions,* $\bar{\mathrm{Cl}}$, $\bar{\mathrm{Br}}$, $\bar{\mathrm{I}}$.

I. *Identification Tests.* 1. Add silver nitrate to potassium chloride, bromide and iodide. Note the colors of the silver salts.

2. Add some iodine dissolved in water, to the following reagents. Repeat the tests with bromine water and then with chlorine water.

(*a*) A few drops of chloroform. Note the color of the chloroform layer. (Test for iodine and bromine.)

(*b*) A starch solution. (This is prepared by putting a *small* pinch of starch into a beaker full of boiling water and boiling the mixture a few minutes.) Note the color produced, if any. (Test for iodine.)

II. *Separation and Determination.* 3. (*a*) Add dilute sulphuric acid to potassium chloride, bromide, iodide separately, and expose the solutions to the air for a long time. What is formed in each case? Which halogen acid is *oxidized* most easily? Which halo-

gen has the smallest electrolytic solution tension (see the chapter on Oxidation and Reduction)? We use the difference in the solution tension to recognize the halogens in the presence of each other; iodide ions are found according to 4 (*a*) or (*b*), bromide ions according to 4 (*b*), chloride ions, in the presence of the other halogens, according to 5.

(*b*) Add chlorine water, a few drops at a time, to a mixture of a drop of a dilute potassium iodide solution with a few c.c. water and some chloroform. Shake the mixture after each addition of chlorine water and add the latter until the violet color of the iodine in the chloroform has disappeared. Read Smith or Remsen on iodine chloride.

4. (*a*) Add dilute sulphuric acid and a little sodium nitrite and starch solution to a mixture of potassium chloride, bromide and iodide (test for *iodides*).

(*b*) Add chlorine water in the same way as in 3(*b*), to a mixture of a drop each of dilute potassium iodide, bromide and chloride solutions, diluted with 2 or 3 c.c. water, and 3 to 5 c.c. chloroform. Add the chlorine water very gradually, shaking the tube after every addition of it, and noting whether a violet chloroform solution is obtained after the addition of the first chlorine water (test for *iodides*). Continue adding chlorine water in the same way gradually until the further addition *does not darken* the *supernatant aqueous layer* by the liberation of more iodine, but if anything makes it paler; then shake the mixture again vigorously and decant the supernatant aqueous layer from the chloroform solution of iodine, which latter is discarded. The aqueous solution contains all the bromide. Add a few c.c. chloroform to it, and continue adding chlorine water slowly as above until the violet color of the chloroform disappears, then observe whether a brown chloroform solution of bromine is formed by the careful addition of more chlorine. (Test for *bromides* in the presence of iodides and chlorides.)

5. Treat a similar mixture of potassium iodide, bromide and chloride with an excess of minium, or better lead dioxide, and acetic acid. Boil the mixture until the odor of iodine or bromine is no longer perceptible, then filter the solution and add silver nitrate and nitric acid to a small part of the filtrate. A pure *white* precipitate is silver chloride. (Test for *chlorides* in the presence

of iodides and bromides.) If the color of the precipitate is not pure white, but even faintly yellow, the bromine or iodine have not been all expelled. The treatment with acetic acid and minium or lead dioxide is continued and repeated until a pure white precipitate results.

6. Ask for an unknown and test it for the three halogens according to 4 and 5.

Oxidation and Reduction Reactions.

I. 1. Add to some ferric chloride solution a few drops of potassium iodide solution and test the mixture for iodine by means of chloroform. The reaction may be written:

$$2\,\overset{+++}{\mathrm{Fe}} + 6\,\overset{-}{\mathrm{Cl}} + 2\,\overset{+}{\mathrm{K}} + 2\,\overset{-}{\mathrm{I}} \rightarrow 2\,\overset{++}{\mathrm{Fe}} + 6\,\overset{-}{\mathrm{Cl}} + 2\,\overset{+}{\mathrm{K}} + \mathrm{I}_2,$$

or, considering only those substances which suffer change:

$$2\,\overset{+++}{\mathrm{Fe}} + 2\,\overset{-}{\mathrm{I}} \rightarrow 2\,\overset{++}{\mathrm{Fe}} + \mathrm{I}_2.$$

The ferric salt is said to be "reduced" to a ferrous salt, the iodide "oxidized" to free iodine. According to the last equation, how can you define "reduction" and "oxidation" in *terms* of *electric* charges? How in terms of the *electron theory?* (Lecture).

2. Treat some ferrous sulphate with bromine water and test the solution for ferric salts by ammonium thiocyanate:

$$2\,\overset{++}{\mathrm{Fe}} + 2\,\overset{--}{\mathrm{SO}_4} + \mathrm{Br}_2 \rightarrow 2\,\overset{+++}{\mathrm{Fe}} + 2\,\overset{--}{\mathrm{SO}_4} + 2\,\overset{-}{\mathrm{Br}},$$

or, again,

$$2\,\overset{++}{\mathrm{Fe}} + \mathrm{Br}_2 \rightarrow 2\,\overset{+++}{\mathrm{Fe}} + 2\,\overset{-}{\mathrm{Br}},$$

the ferrous salt being "oxidized" to a ferric salt, the bromine[1] "reduced" to a bromide ion. Amplify your definitions of oxidation and reduction to include the results of this test. Can there be any reduction without a simultaneous oxidation, or *vice versa?*

3. Connect the oxidation and reduction effects with electrical changes by using an electric current to reduce ferric salts, and likewise to oxidize ferrous salts.

(*a*) Place a 10 c.c. beaker inside a larger beaker, fill both with

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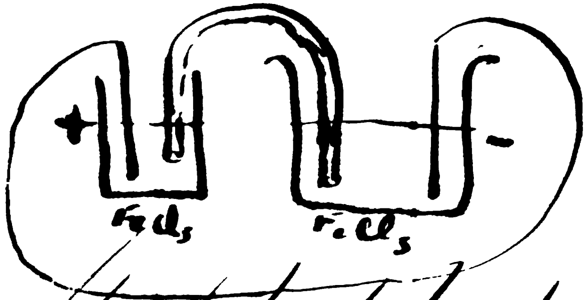
[1] It is very likely that the real reaction is $2\,\overset{++}{\mathrm{Fe}} + \overset{+}{\mathrm{Br}} \rightarrow 2\,\overset{+++}{\mathrm{Fe}} + \overset{-}{\mathrm{Br}}$. *Vide* W. A. Noyes, *Journal of the Am. Chem. Soc.*, **23**, 460 (1901), and Stieglitz, *ibid.*, **23**, 796 (1901), and Walden, Zeitschrift für Physikalische Chemie, **43**, 385 (1903).



~~$2\,FeCl_3 \rightarrow 2\overset{+++}{Fe} + 6\bar{Cl} \rightarrow$~~

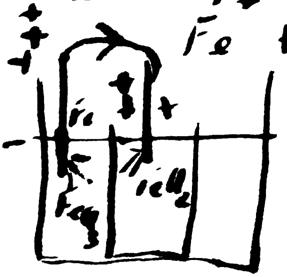
$FeCl_3 \Rightarrow Fe\bar{|} + Cl|^{+}$

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

$FeCl_2 \Rightarrow Fe\bar{|} + Cl\bar{|}^{+}$

~~Fe~~ $FeCl_2 + Cl \rightarrow FeCl_3$

$\overset{++}{Fe} + 2\bar{Cl} + \overset{+}{\bar{Cl}} \rightarrow \overset{+++}{Fe} + 3\bar{Cl}.$



FeCl3

a dilute solution of ferric chloride (best acidified with a little hydrochloric acid to prevent a reduction to metallic iron), which must more than cover the smaller beaker. Now pass not too strong an electric current through the solution (Instructor), dipping the *negative* electrode into the smaller beaker, the positive electrode into the larger one. After a few minutes, pipette some of the liquid out of the small beaker *from next to the negative electrode* and test it for ferrous iron with potassium ferricyanide.

(*b*) (*a*) may be repeated with a freshly prepared solution of ferrous chloride, fine iron wire being dissolved in hydrochloric acid. The *positive* electrode is placed in the inner beaker and the solution around it is tested for ferric iron with ammonium thiocyanate.

4. Confirm the conclusions arrived at in 3 by *producing an electric current* from reaction 1 or 2.[1]

(*a*) Place in one 50-c.c. beaker a dilute solution of ferric chloride and in a second 50-c.c. beaker of the same height, a solution of sodium chloride, and join the two beakers by a small U-tube filled with the sodium chloride solution and closed snugly with rolls of filter paper moistened with the sodium chloride solution. A platinum electrode (storeroom) is dipped into each of the solutions and the electrodes are connected with a sensitive voltmeter or galvanometer (Instructor) to test whether a current is passing, connecting the ferric solution with the *positive* post. Note whether even a very slight current passes. Then add a little potassium iodide *to the beaker containing sodium chloride*, stir the mixture and note the passage of a strong current and its *direction*. (Lecture.)

(*b*) (*a*) may be repeated using ferrous sulphate in place of potassium iodide, and bromine water in place of ferric chloride. *Note the direction of the current.*

5. (*a*) Treat a little potassium chromate with some dilute sulphuric acid and an excess of potassium iodide, and test a part of the solution for free iodine by means of chloroform. Boil away the iodine. What does the color of the solution now show as to the action of the iodide on the chromate? (Chromium, p. 14, 1 (*c*).) Considering valence (see Chromium, 1) as an electric charge or a

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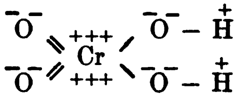
[1] Ostwald, Zeitschrift für Physikalische Chemie, 9549 (1894).

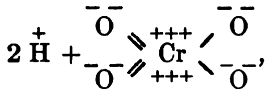
possible or "potential" electric charge, we have for chromic acid:


(1)

and for the fully hydrated molecule:

$$\overset{+++}{\underset{+++}{\mathrm{Cr}}}\ (\overset{--}{\mathrm{O}} - \overset{+}{\mathrm{H}})_6. \qquad (2)$$

It could ionize, besides as an acid according to:



or

$$2\,\overset{+}{\mathrm{H}} + \mathrm{Cr}\overset{--}{\mathrm{O}_4} \qquad (3)$$

also to a *very slight* extent as a *base*, according to

$$\overset{+++}{\underset{+++}{\mathrm{Cr}}}\ (\overset{--}{\mathrm{O}}\overset{+}{\mathrm{H}})_6 = \overset{+++}{\underset{+++}{\mathrm{Cr}}} + 6\,\bar{\mathrm{O}}\mathrm{H}. \qquad (4)$$

Quite independently of any views as to the nature of valence in the non-ionized molecules, chromic acid anhydride may be considered to form with water a hydrate ionizing amphoterically as an acid and slightly as a base. (Which *pronounced acid* have we already found to give plain evidence of faint *basic* properties?) The basic ionization of chromic acid may be expressed in:

$$\mathrm{CrO_3} + 3\mathrm{H_2O} \rightleftarrows \mathrm{Cr\ (OH)_6} \rightleftarrows \overset{++++++}{\mathrm{Cr}} + 6\bar{\mathrm{O}}\mathrm{H} \qquad (4a)$$

Considering that when chromic acid oxidizes hydriodic acid and other compounds we obtain chromium salts, in which chromium appears as a trivalent positive ion, we can write the oxidation reaction

$$2\,\mathrm{H_2CrO_4} + 12\,\mathrm{HI} \rightarrow 2\,\mathrm{CrI_3} + 3\,\mathrm{I_2} + 8\,\mathrm{H_2O};$$

also:

$$2\,\overset{+++}{\underset{+++}{\mathrm{Cr}}} + 12\,\bar{\mathrm{O}}\mathrm{H} + 12\,\overset{+}{\mathrm{H}} + 12\,\bar{\mathrm{I}} \rightarrow 2\,\overset{+++}{\mathrm{Cr}} + 6\,\bar{\mathrm{I}} + 3\mathrm{I_2} + 12\,\mathrm{H_2O}; \quad (5)$$

and, only those atoms or ions which change their charges being considered, equation (5) becomes simply:

$$2\,\overset{+++}{\underset{+++}{\mathrm{Cr}}} + 6\,\bar{\mathrm{I}} \rightarrow 2\,\overset{+++}{\mathrm{Cr}} + 3\,\mathrm{I_2}. \qquad (6)^1$$

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[1] See footnote 1, page 44.

Considering the fundamental equations 4 (*a*) and (6), in which solution should the oxidation effect be strongest, — in neutral, alkaline or acid solution? In which solution would we have most hexivalent chromium ions?

(*b*) Confirm the plausibility of these conceptions by producing an electric current by the reaction, going in the direction foretold by equation (6) (the *positive* current from the chromic acid) and growing in intensity under the conditions foretold. Place in one 50-c.c. beaker, as in 4(*a*), a little potassium chromate solution, fill the second beaker with dilute potassium iodide solution, connect the two with a bridge filled with sodium chloride solution. Connect the electrodes with the voltmeter and observe whether a current passes. Then add dilute sulphuric or hydrochloric acid gradually to the beaker containing the chromate and observe the behavior of the needle.

Add a few cubic centimeters of starch solution to the beaker containing the iodide, while the current is passing. What is shown *next to the platinum plate?* Recall the analogous lecture experiments with permanganate and ferrous salts. Recall the formation of $\overset{+++++}{As}$ and the precipitation of As_2S_5 from *strong acid* solutions (p. 36, Arsenic, 2 (*b*)). What evidence does this give that a *strong* acid like arsenic acid also ionizes *a little* as a base?

II. 1. Add to ferric sulphate solution some potassium chloride and test it with ferricyanide for a ferrous salt. Compare the result with that obtained in I, 1 (p. 44). Does the reaction proceed measurably in the same way?

2. (*a*) Dip into mercuric nitrate solution some copper wire, after a few seconds remove the copper and rub it gently. Add some zinc to copper sulphate. Express the reactions in equations as simple oxidation and reduction reactions.

(*b*) Dip your platinum wire into copper sulphate solution. Is copper visibly deposited? *Oxidation and reduction must depend, according to* 1 *and* 2, *therefore, on some further property beyond the mere qualitative possibility of the transfer of electrical charges.* (See IV.)

III. 1. Dip a pair of platinum electrodes (storeroom) into a copper sulphate solution and pass a current through the solution. Copper is deposited. Then reverse the current. Note that the precipitated copper is redissolved.

2. Considering then that the reaction

$$\mathrm{Cu} \rightleftarrows \overset{++}{\mathrm{Cu}}$$

is reversible, what condition of equilibrium should ultimately establish itself at the surface of metallic copper dipping into a solution containing more or less copper ions? (Lectures on Solution Tension.) If we consider the pure metallic copper to have a constant concentration, what should be true of the concentration of copper ions on its surface in any such solution in a condition of equilibrium?

3. This characteristic constant concentration of copper ions surrounding copper in such a condition of equilibrium may be called its *solution tension constant*,[1] which may be measured in terms of gram ions per liter or in the equivalent *osmotic* pressure of these gram ions per liter (one gram ion or gram molecule of any substance per liter has an osmotic pressure of twenty-two atmospheres at 0°). Each metal ion has its own characteristic concentration for equilibrium with its metal, or a solution tension constant, — for instance, for copper it is of the order $\frac{5}{10^{22}}$ gram ion per liter,[2] for zinc 5×10^{16}. Similar relations apply to negative ions, as the chlorine ion and iodine ion. (See p. 43, II, 4 (*b*).)

4. (*a*) How will equilibrium establish itself on the surface of metallic copper according to 3 if it is dipped into a solution containing no copper ions? (Lecture on Helmholtz's "double layer.")

(*b*) Will a "double layer" form if copper is dipped into a solution containing $\frac{5}{10^{22}}$ gram ions copper per liter? Will the copper be electrified?

Will it be experimentally possible to dip zinc into a solution containing 5×10^{16} gram ions zinc per liter? Can zinc of itself be anything but negatively charged in its own salt solutions?

(*c*) If copper is dipped into a stronger sulphate solution than one containing $\frac{5}{10^{22}}$ gram ions copper per liter, what charge will the metal acquire through the formation of a "double layer"? How does this reduce the concentration of copper ions *at the*

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[1] Nernst, *Zeitschrift f. physikalische Chemie*, **4**, 150 (1889).

[2] Jones, Elements of Physical Chemistry, p. 475.

surface to the required constant to produce equilibrium? What must happen if we connect the metallic copper with any negatively charged body in this case? (See III, 1.) Will the result be any different if we dip metallic zinc into copper sulphate?

(*d*) Place 10 c.c. copper sulphate solution in each of two 100-c.c. beakers, dilute each solution with 50 c.c. sodium chloride solution, introduce copper electrodes connected with a voltmeter, and connect the solutions with a salt bridge. Is a current produced? Add to the beaker connected with the negative post of the voltmeter sodium hydroxide to precipitate copper hydroxide. Explain the effect on the voltmeter. Add an excess of sodium hydroxide and again explain the effect (recall the "solubility-product"). Add ammonium sulphide and explain the result again. Add potassium cyanide to dissolve the copper sulphide and explain the result again.[1] (Recall the stability constants of complex ions.)

(*e*) Dip into two copper sulphate solutions as in (*d*) a pair of copper electrodes and connect them with the voltmeter. Replace one of the electrodes and one of the solutions by a zinc electrode dipping into a zinc sulphate solution; in what direction must and does the current go? Compare the result with that obtained in II, 2 (*a*), p. 47.

5. Judging by 4 (*a*) to (*e*), what metals will ordinarily replace (reduce) each other according to their solution tension constants? Develop the *limit* to this general principle as follows:

(*a*) If copper is dipped into copper solutions containing say $\frac{5}{10^{22}}$ gram ions copper per liter, will it acquire an electric charge (see 4 (*b*))? If we imagine zinc dipped into a solution containing 5×10^{16} gram zinc ion per liter, will it be in equilibrium with its solution? Will it acquire an electric charge? If we imagine the copper and zinc solutions united (without diluting) and dip the copper and zinc rods into the mixture, will either be other than in equilibrium with its ions? If so, will either be electrified? Will zinc be able to precipitate copper under these circumstances?

(*b*) If in this mixture we imagine the copper ion *reduced in concentration*, the copper will acquire a negative charge (4(*a*)). If it is connected with the zinc rod, and the zinc acquires the negative charge, can the zinc still be in equilibrium with its ion? What will happen to some zinc ions? and to the copper rod? Under what conditions then should a metal (Cu) with a *lower* solution tension precipitate a metal (Zn) with a higher solution tension?

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[1] Küster, Zeitschrift für Elektrochemie, 4, 503 (1898).

(*c*) For the imaginary condition of equilibrium established in (*a*) for two metals and their solutions, when both are in equilibrium and neither will replace the other, the concentration of each metal ion in solution has its characteristic constant value for the solution tension (see 3, p. 48) of the metal; the proportion of the concentrations is therefore also a constant:

$$\frac{\overset{++}{\text{Zn}}}{\overset{++}{\text{Cu}}} = \frac{5 \times 10^{16}}{\frac{5}{10^{22}}} = 10^{38} = \text{K}.$$

For $\overset{++}{\text{Cu}} + \text{Zn} \rightleftarrows \overset{++}{\text{Zn}} + \text{Cu}$ *we have equilibrium whenever this constant* K is fulfilled, i.e., whenever the relative concentrations are as 10^{38}: 1. It can be shown that this is a general relation, equilibrium existing between the two metals whenever their concentrations are in the given proportions.[1] What must happen, accordingly, if more zinc ions are added and the proportion is exceeded? or if copper ions are suppressed and the proportion exceeded?

Recall the lecture experiments on the direction of the current in a battery composed of zinc dipping into zinc sulphate solution, copper into copper sulphate and on the *reduction* and *final reversal* of the current by the successive additions of sodium hydroxide, ammonium sulphide and of potassium cyanide to the copper sulphate solution and the consequent suppression of the copper ions.[2]

(Recall also the lecture experiments on the precipitation of gold by mercury and on the reversal of the reaction and the precipitation of mercury by gold when the gold ions are suppressed by potassium cyanide, forming the very stable complex gold cyanide ions.)[3]

(*d*) Apply the principle developed in (*c*) to explain why zinc will dissolve readily in hydrochloric acid and only in traces in water, the solution tension constant for zinc being considerably larger

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[1] The theory and its mathematical development we owe to Nernst.

[2] Kuester, *loc. cit.*

[3] Bodlaender, *loc. cit.*

than that of hydrogen. What essential difference is there between water and hydrochloric acid? How will the solution of traces of zinc in water with the formation of traces of practically completely ionized zinc hydroxide accentuate this difference? Why will sodium nevertheless dissolve in water, when zinc will not?

IV. 1. Judging by the facts developed in II and III, under what conditions will one metal reduce the ion of another metal? *Briefly, what constants and what variables are involved?*[1]

2. Reductions and oxidations in general are subject to essentially the same principles and are most likely all more or less reversible.

(*a*) Recall the reduction of ferric ions by iodine ions (I 1 and 4).

(*b*) Can ferrous salts be partially oxidized to ferric by iodine? (Lecture-experiment.) We have, therefore:

$$2\,\overset{+++}{\mathrm{Fe}} + 2\,\overset{-}{\mathrm{I}} \rightleftarrows 2\,\overset{++}{\mathrm{Fe}} + \mathrm{I}_2.$$

3. (*a*) Place in one of a pair of beakers some formalin diluted with sodium nitrate, in a second one some silver nitrate solution, connect the two with platinum electrodes and a voltmeter, and with a sodium nitrate bridge — note the potential shown. Add sodium hydroxide to the formalin mixture, and note the change. Add ammonia to the silver nitrate, and note the change.

(*b*) Mix in another beaker silver nitrate and a few drops of formalin. In a fourth beaker mix silver nitrate, ammonia and sodium hydroxide and add formalin. Is the *oxidation* of *organic compounds* essentially different in principle from that of inorganic substances? What are probably the real oxidizing ingredient and the real reducing agent in this action? (Lecture.)

Hydrocyanic Acid, HCN; *Cyanide Ion* ($\overline{\mathrm{CN}}$).

NOTE.— Particular care must be taken with this acid on account of its poisonous character. Its fumes should not be inhaled, a strong acid should not be used on its salts, and care should be taken not to cut the hands while it is used. Note its faint but characteristic odor in the air (*do not inhale it directly*).

1. Add potassium cyanide gradually to silver nitrate until no further change occurs. Recall 1 (*c*) (p. 29) under copper and ex-

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[1] For a more complete discussion of solution tension see Nernst's Theoretical Chemistry or Le Blanc's Electrochemistry.

plain why the precipitated silver cyanide redissolves in an excess of the reagent. Would a few drops of silver nitrate added to potassium cyanide, failing ~~to give a precipitate~~, be ~~any~~ reliable evidence of ~~the absence~~ of ~~cyanide~~?

2. Carry out the two following experiments side by side:

(*a*) To a few drops of potassium cyanide add a little ferrous sulphate and a few drops of ferric chloride and some sodium hydroxide. Warm the mixture and then add hydrochloric acid. (*Characteristic test for cyanides.*) What is the precipitate? Add sodium hydroxide to it.

(*b*) Repeat every step of (*a*), but *leave out the cyanide entirely.*

For the identification of a cyanide ion by this method, the complex ferro- or ferricyanide ion must be *prepared* in *alkaline* solution, and then *tested* for in *acid* solution.

3. To a drop of potassium cyanide solution, add 2 c.c. of yellow ammonium sulphide, evaporate the mixture to dryness on the steam-bath and add ferric chloride and hydrochloric acid to the residue dissolved in water (*characteristic test for cyanides*).

4. (*a*) Try 1 and 2 (*a*) with a fresh solution of mercuric cyanide.

(*b*) Add sodium hydroxide to mercuric nitrate and then to the cyanide. What is peculiar in the behavior of this cyanide? To what are the peculiarities due? Recall the conductivity of mercuric cyanide solution (Lecture).

(*c*) Add hydrogen sulphide and some hydrochloric acid to mercuric cyanide. What does this test show? How would you proceed to identify cyanogen in mercuric cyanide?

Thio, $HSCN$, *Ferro-,* $H_4Fe(CN)_6$, *Ferricyanic,* $H_3Fe(CN)_6$, *Acids.*

1. What metal ions are identified by these acids? How would you test for the acids?

2. Add silver nitrate to a salt of each acid.

Hydrogen Sulphide, (Hydrosulphuric Acid), H_2S. *Sulphydric and Sulphide Ions* ($\overset{-}{S}H$ *and* $\overset{=}{S}$).

1. Treat each of the following sulphides with dilute and concentrated hydrochloric acid and test with a strip of filter paper moistened with ammoniacal silver nitrate or sodium plumbite whether hydrogen sulphide is evolved: The sulphides of iron,

lead, arsenic, mercury. Recall the behavior of the metal salts to hydrogen sulphide and hydrochloric acid.

2. At the sealed end of a narrow glass tube put a mixture of mercuric sulphide and dry sodium carbonate, cover it with a layer of the carbonate, heat the latter first and then the mixture. Extract the cooled mass with water and test the filtrate for a sulphide according to 1.

3. Treat some sulphide with a little aqua regia. Boil the mixture, dilute it with a very large amount of water and add barium chloride. What is formed?

4. Add a drop of hydrogen sulphide water and some sodium hydroxide to potassium nitroprussiate.

Nitric Acid, HNO_3. *Nitrate Ions,* ($N\bar{O}_3$).

1. Heat in a narrow glass tube, sealed at one end, some lead nitrate; some potassium nitrate. If gases are evolved identify them.

2. (*a*) Add a drop of sodium nitrate solution to a mixture of 2 c.c. water and 2 c.c. concentrated sulphuric acid, cool the mixture and cover it carefully with a layer of 5 c.c. ferrous sulphate solution. Observe the zone of contact against white paper. (*Characteristic test,* but note § 4.)

(*b*) Repeat (*a*), but use the ferrous sulphate solution by adding a few drops at a time and shaking the mixture.

(*c*) Repeat (*a*), using a drop of potassium iodide in place of the nitrate. Note your conclusions as to the right method of testing for a nitrate according to (*a*).

3. Add some zinc and iron dust to a drop of sodium nitrate solution dissolved in a few c.c. sodium hydroxide solution. Heat the mixture and test the vapor for ammonia. How could this test be used in the presence of an ammonium salt? Explain the reaction.

4. (*a*) Use a drop of potassium *nitrite* solution for 2 (*a*). Would it also give 3?

(*b*) Add dilute acetic acid to a potassium nitrite solution. Then add a drop of potassium iodide and chloroform. (Differences from nitrates.)

Chloric Acid, $HClO_3$; *Chlorate Ion* ($Cl\bar{O}_3$).

1. (*a*) Add silver nitrate to a potassium chlorate solution.

(*b*) Heat some dry potassium chlorate in a narrow glass tube; test the gas evolved. Dissolve the residue in water and add silver nitrate and some nitric acid to this solution.

2. Drop a *little* potassium chlorate on a piece of charcoal heated to redness before the blow-pipe.

3. Add a *very little* potassium chlorate (a few crystals) to a drop or two of concentrated sulphuric acid in a porcelain dish. (Care! the gas evolved is explosive!) Note the color and odor of the gas and its action on litmus paper. (Larger quantities of chlorate can produce very dangerous explosions with concentrated sulphuric acid!)

Sulphuric Acid, H_2SO_4. *Sulphate Ion* ($\bar{S}\bar{O}_4$).

1. (*a*) Add barium chloride to sodium sulphate and then add a little dilute hydrochloric or nitric acid. Since all other ordinary barium salts[1] are soluble in dilute acid, sulphate ions can be readily identified by this test. Precautions against error are given in (*b*) and (*c*).

(*b*) Add barium chloride to a few c.c. concentrated hydrochloric acid. What is the precipitate and why is it formed? How can it be distinguished from the precipitate obtained in (*a*)?

(*c*) Repeat (*b*) using nitric acid in place of hydrochloric acid. Considering (*b*) and (*c*), how must the test for sulphate ions according to (*a*) be carried out to avoid error?

2. Reduce some barium sulphate on the end of a platinum wire in the reducing zone of a Bunsen burner, cool it in the inner zone and then add the mass to a drop of hydrochloric acid on a watch-crystal. Note the odor. Give the reaction equation.

NOTE. — As illuminating gas contains some sulphur, an alcohol flame is better for this test in important work.

3. Which two negative ions does sulphuric acid form? Which is formed more readily in the presence of very little water? of much water? Add some barium sulphate to a c.c. concentrated sulphuric acid; warm the mixture. Then cool it and pour a few drops of the clear, supernatant liquid into a beaker full of water. (Care!) Explain the result.

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[1] *Vide* Fresenius, p. 327, in regard to barium fluorosilicate.

Hydrofluoric Acid, H_2F_2. *Fluoride Ion* $(\bar{\bar{F}}_2)$.

1. Cover one surface of a watch-crystal with a film of paraffin remove part of the paraffin from the glass by writing with a sharp pointed glass rod or pin on it, and expose the prepared surface to the fumes of hydrofluoric acid obtained from a mixture of calcium fluoride and concentrated sulphuric acid in a lead dish (storeroom). The dish should be placed in a warm but not hot place.

2. Mix a little fluorspar with silica in a dry test-tube, fit the latter with a perforated cork carrying a narrow glass tube. Put some concentrated sulphuric acid into the test-tube and a *drop* of water into the narrow tube in the cork. Warm the contents of the test-tube gently, and observe the drop of water in the narrow tube. Read Smith or Remsen on silicon tetrafluoride. This is the most convenient *test for a fluoride.*

Silicic Acids.[1]

1. Mix a little silica with some fluorspar and concentrated sulphuric acid in a lead dish with a perforated lead cover, hold a drop of water in the loop of a platinum wire over the opening in the cover and warm the dish very gently.

2. Heat a particle of glass or of sand in a metaphosphate bead, and note the insoluble silica "skeleton." Recall the chemistry of the metaphosphate bead. (Lecture.)

3. Treat a solution of sodium silicate with hydrochloric acid in excess. Whether a precipitate is formed or not, evaporate the mixture to dryness on the steam-bath, and then heat the dried residue 40 to 60 minutes longer on the steam-bath. Add dilute hydrochloric acid. The insoluble residue is the so-called "insoluble silicic acid." This behavior gives us the most convenient *test for silicic acid.*

4. Pulverize a piece of glass or of porcelain, mix the powder with equal parts of dry sodium and potassium carbonate and fuse the mixture in a small platinum dish (Instructor). Extract the mass with water, acidify it with hydrochloric acid and proceed as in 3.

Carbonic Acid H_2CO_3. *Carbonate Ion,* $(\bar{C}\bar{O}_3)$.

Treat any carbonate with hydrochloric or nitric acid. Decant the evolved gas into a test-tube containing several c.c. lime-water, and then shake the latter, after closing the tube with the thumb. If the gas is evolved slowly, pass it through a tube into lime water.

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[1] See Smith, page 524.

Chromic Acid. Chromate Ion,[1] $(\overline{\mathrm{Cr}}\overline{\mathrm{O}}_4)$.

1. Treat potassium chromate with hydrochloric acid and hydrogen sulphide. To what is the change of color due? Write the equation for the reaction from the electric point of view.

2. (*a*) Add silver nitrate to potassium chromate.

(*b*) Dilute a mixture of sodium chloride and potassium chromate, and determine the relative solubility of the silver salts.

3. Prepare some hydrogen peroxide from barium peroxide and dilute hydrochloric or sulphuric acid. Add to a few c.c. of water a drop or two of potassium bichromate solution, a drop of dilute hydrochloric acid and several c.c. of ether; then add some of the hydrogen peroxide solution and shake the mixture. This is a characteristic test for chromic acid and for hydrogen peroxide.

Boric Acid. Borate Ion,[2] $(\overline{\mathrm{B}}\overline{\mathrm{O}}_{\overline{3}})$.

1. Make a rather concentrated solution of borax in water, and add to a part of it some silver nitrate. The white precipitate is silver borate. Then dilute one or two c.c. of the borax solution with 50 c.c. of water, and add silver nitrate to it. What is the brown precipitate and to what action of water on borates does it owe its formation? Why does water have this action on sodium tetraborate?

2. Dip a piece of turmeric paper in a borate solution, dry the paper on a watch-crystal over a steam-bath, moisten it with dilute hydrochloric acid and dry it again. The red tint produced is a very characteristic *test for boric acid.*

3. Add to a few drops of a borate solution in a porcelain dish 10 c.c. concentrated sulphuric acid and 10–20 c.c. alcohol and light the alcohol. The green edged flame is characteristic for *boric acid* in the absence of copper and of chlorides.

4. Mix a crystal of a borate with a little ammonium fluoride in a mortar (Care! Do not get the fluoride on the fingers!) and heat a little of the mixture on the platinum wire in the Bunsen flame. (Spectrum, Vogel's Spectral Analyse, p. 294.)

Arsenious Acid, H_3AsO_3, *and Arsenic Acid,* H_3AsO_4.

See Arsenic, p. 35.

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[1] (*See also Chromium,* p. 14.) See Smith or Remsen on Bichromic Acid.

[2] Read Smith or Remsen on the various boric acids.

Phosphoric Acid,[1] H_3PO_4 *and the Phosphate Ion,* $\bar{P}\bar{O}_4^{-}$.

1. For what metal ion did you use the phosphate ion as a qualitative test? Vice-versa, use a solution of the same metal ion, under the proper conditions (in the presence of ammonia and ammonium chloride or nitrate) as a test for the phosphate ion. Although the precipitate is characteristic (except that arsenic acid gives a perfectly similar one), the test can be used only in alkaline solutions, and as most phosphates are insoluble in such solutions, the test is not a very convenient one.

2. Dissolve a little calcium phosphate in nitric acid, add 10 or 20 c.c. ammonium molybdate solution and let the mixture stand in the cold for five minutes. Then warm it gently. The precipitate is ammonium phosphomolybdate, $(NH_4)_3PO_4$, $12MoO_3$. Conforming to its composition, the precipitate always requires a large excess of the molybdate solution for its formation.

Let the precipitate subside, decant the liquid, wash the precipitate twice by decantation, dissolve it in a few drops of ammonia and add some magnesium nitrate or sulphate solution. Bring the precipitated magnesium ammonium phosphate on a very small filter, wash it with some water, dissolve it in a little acetic acid, add silver nitrate to the solution and cover the mixture with a layer of dilute ammonia: at the junction a zone of yellow silver phosphate will appear.

The molybdate test is the most valuable test for phosphates because it can be carried out in acid (nitric) solution: most phosphates that are insoluble in water dissolve in nitric acid. The subsequent tests with magnesium and silver salts are confirmative tests. Arsenic acid, H_3AsO_4, gives a similar arsenomolybdate (p. 36), which is formed only when the mixture is strongly heated (difference from phosphate test). It gives a red silver arsenate. If arsenic is present, it is best removed by precipitation with hydrogen sulphide before the phosphate test is made.

Organic Acids.

Mix a salt of any organic acid with an equal amount of cupric oxide powder, put a little of the mixture into the sealed end of a narrow glass tube four inches long, heat the open end of the tube and draw it out to a rather wide and long capillary bent at a right angle to the tube. Cut off all but two or three inches of the capillary. Then heat the copper oxide mixture slowly and pass any evolved gases into lime water, using the capillary as the delivery tube.

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[1] Read Smith or Remsen on meta- and pyrophosphoric acids.

All organic compounds (as well as most carbonates) give this test. Carbonic acid can, of course, be first removed, if present.

Of the large number of organic acids, only four very common ones, representing typical groups, will be studied.

Acetic Acid, CH_3COOH. *Acetate Ion,* $(CH_3\bar{C}O_2)$.

1. Mix acetic acid with two volumes of alcohol, add an equal volume of concentrated sulphuric acid (Care!), mix the liquids and warm them gently. Compare the odor of the product (ethyl acetate) with that of a fresh mixture of acetic acid and alcohol.

Oxalic Acid, $H_2C_2O_4$. *Oxalate Ion* $(\bar{C}_2\bar{O}_4)$.

1. Add some calcium chloride to ammonium oxalate, then acidify the mixture with acetic acid. Calcium oxalate and calcium fluoride are the only common calcium calts insoluble in acetic acid.

2. Treat ammonium oxalate with dilute sulphuric acid and then add some finely powdered manganese dioxide. What gas is evolved? Write the reaction equation. This is a most convenient test for an oxalate.

Tartaric Acid, $C_4H_6O_6$.

1. Heat some sodium potassium tartrate (Rochelle salt) on the lid of a porcelain crucible. Note the odor of the vapors.

2. (*a*) Add a little sodium hydroxide to copper sulphate and to some aluminium sulphate solutions.

(*b*) Repeat (*a*), but before the addition of the alkali add an excess of a concentrated solution of Rochelle salt to the copper and aluminium sulphates. (Recall the lecture experiments on complex metal ions with tartrates.)

(*c*) To determine whether metal ions are completely suppressed (*cf.* the stability constant of complex ions) add ammonium sulphide to the mixture of copper sulphate and Rochelle

salt and see if the extremely insoluble copper sulphide can be precipitated.

Important Note. — Many organic substances containing so-called "alcohol" groups (Lecture), such as tartrates, citrates, sugars, etc., behave like Rochelle salt in suppressing metal ions, and many metal ions, such as chromium, ferric, ferrous, nickel, manganese, barium, calcium ions, etc., form complex ions with these organic compounds. The latter interfere therefore with the precipitation of all but the least soluble salts. As only the heavy metal sulphides and a few other common salts are sufficiently insoluble to be precipitated completely under such conditions, it is usually necessary to destroy these organic compounds after the precipitation of the silver, copper and arsenic groups, and before testing for aluminium, etc.

3. (*a*) Add some calcium chloride, ammonium chloride and ammonia to a solution of Rochelle salt. Bring the precipitate on a filter and wash it well with water.

(*b*) Put a stick (two inches) of solid sodium hydroxide in a test-tube, cover it with water and after a few moments pour away the solution of the outside crust, which usually contains considerable carbonate. Dissolve the rest of the sodium hydroxide in a little water. Then treat the larger part of the calcium tartrate obtained in (*a*) with this sodium hydroxide solution. It will dissolve as the sodium salt of the complex calcium tartaric acid ion ($Na_2C_4H_2(O_2Ca)O_4$). Dilute the solution and boil it. Calcium tartrate is reprecipitated (characteristic test).

(*c*) To a very small portion of the calcium tartrate obtained in (*a*) add four or five drops of silver nitrate solution and a few drops of ammonia. Boil the mixture vigorously in a test-tube, allowing it to evaporate nearly to dryness, to obtain a silver mirror

Salicylic Acid. $C_6H_4(OH)COOH$.

1. To a solution of sodium salicylate add:

(*a*) Some hydrochloric acid.

(*b*) Some ferric chloride.

(*c*) An equal volume of methyl alcohol and of concentrated sulphuric acid. (Care!) Heat the mixture and note the odor produced.

PART III.

SYSTEMATIC ANALYSIS

A. Preliminary Examination

The unknown, if it is a solid other than a metal or alloy, should be reduced to a coarse powder: it is advisable to pulverize a very small trial portion first, as a safeguard against mixtures which may explode as the result of friction or concussion.

Before the systematic wet analysis is undertaken, it is advisable to subject the substance to a few short preliminary tests, which may throw considerable light on its nature and may facilitate the rigorous analysis. Of these preliminary tests particular attention should be paid to the following results, as they modify the course of the subsequent systematic analysis. For the same reason these three tests, at least, should never be omitted, unless the appearance of the substance makes them obviously unnecessary. (1) *Carbonization* in the *dry heat test*, with the emission of the odor of burnt organic matter indicates the presence of organic substances, which without due precautions *may interfere with the detection of some of the metals of the third and second groups* (see p. 59). The precautions given in the systematic part are then observed (pp. 72, etc.). (2) If a *silicate* is shown to be present in quantity by the metaphosphate bead test (p. 63), the special method of analysis for *silicates* should be followed (p. 84). (3) If *cyanogen* compounds are clearly indicated by the preliminary tests, and the compounds are insoluble, students should use the special method for the analysis of cyanogen derivatives, Fresenius, p. 529. The comparative stability of the complex ions of many metals with cyanogen and their salts renders this course advisable.

I. *The Substance is a Non-metallic Solid.*

1. *Heat* a little of the solid substance in the sealed end of a narrow glass tube three inches long. Note all changes, as indicated in the following sub-heads. If in doubt as to the interpre-

tation of the result, proceed with the analysis — the tests are largely *indications*, and the wet analysis will ultimately remove the doubt.[1]

Observation and Test.	Conclusion.
(1) A gas is formed.	
(a) Brown, odor of NO_2	Nitrates.
(b) Brown, odor of Br	Bromides.
(c) Violet	Iodides.
(d) Yellow, odor of chlorine	Chlorides.
(e) Inflammable, blue flame	CO, oxalates, etc.
(f) Inflammable, crimson flame	*Cyanogen* from *cyanides*.
(g) Odor of SO_2	Sulphur derivatives.
(h) Odor of HCN	*Cyanides*.
(i) Odor of H_2S	Sulphides, etc.
(j) Odor of ammonia. Litmus	Ammonium salts, *cyanides*.
(k) Glowing splinter ignites	Oxygen, from the oxide of a noble metal, a higher oxide, a peroxide,[2] chlorate, nitrate.
(l) Drop of lime water, cloud.	Carbonates, *organic compounds*.
(m) Steam. Colorless liquid condenses.	Water, mechanical, crystallization, or constitutional.
(2) A sublimate is formed.	
(a) White. Lime test, NH_3	Ammonium salts.
(b) White, sublimes without fusing, yellow, while hot.	HgCl.

*Illustration:**

No.	Substance.	Reagent.	Observations.	Conclusion.
1	Unknown 1	Dry heat	Undecided	
2	Do	Blow-pipe	Brown incrustation	Cd
3	Do	Metaphosph. bead.	Undecided	
4	Do	H_2O	Neutral solution	
5	Solution ... 4#	HCl	No precipitate	Absence of Ag, etc.
6	Do ..... 5#	H_2S	Yellow precipitate	Cd, As, Sn.
7	Precipitate 6#	$(NH_4)SH$	Insoluble	Cd

The numbers 4, etc., refer to the solution (precipitate, filtrate), *obtained* in *line* 4, 5 or 6.

* The forms of this table and of those in the text are analagous to those used by W. A. Noyes.

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[1] *A record should be kept of each analysis according to the following method. The observations and conclusions should be recorded while the analysis is being made, not after its completion.* The instructors will not consider any other kind of a report.

[2] BaO_2 is a *peroxide*, a salt of hydrogen peroxide; MnO_2 and PbO_2 are *dioxides*.

Observation and Test.	Conclusion.
(2) A sublimate is formed.— *Continued*	
(c) White, fuses	$HgCl_2$.
(d) White, fuses to a yellow liquid.	Sb_2O_3.
(e) White, brilliant crystals	As_2O_3.
(f) White, combustible vapors.	*Organic* acids.
(g) Metallic globules	Hg, from oxide, etc.
(h) Yellow or yellowish brown, inflammable with SO_2 odor.	S.
(i) Yellow	As_2S_3.
(j) Yellow, red by rubbing	HgI_2.
(k) Black, violet vapor	I.
(l) Black, colorless vapor	As (mirror-like).
(m) Black, red by rubbing	HgS.
(3) The substance changes color and turns:	
(a) Black, odor of burnt organic matter, organic gases, H_2O.	*Organic* substances.
(b) Black, without signs of organic matter.	Black metal oxide, e.g. of Cu, Ni, Co, Mn, etc.
(c) Yellow; cooled, white	ZnO.
(d) Yellowish-brown; cooled, light yellow.	SnO_2.
(e) Brown-red. Fuses easily. Cooled, yellow.	PbO.
(f) Orange. Fuses, but with difficulty. Cooled, pale yellow.	Bi_2O_3
(g) Dark brown, hot and cooled.	Mn_3O_4.
(h) Dark brown, cooled, reddish.	CdO.
(i) Dark red to black, cooled red.	F_2O_3.

2. Treat a mixture of the substance and sodium carbonate with the *blow-pipe flame*. The effect of the reducing flame is given, unless the oxidizing flame is specified. Note any metal bead that may form in the cavity as well as any incrustation around the cavity. Metallic globules should be examined in regard to brittleness, malleability and color. If no larger globules are seen, the contents of the cavity are crushed in a mortar, carbon and soluble matter washed away by decantation, and any residue vigorously rubbed: mortar and pestle are then examined for glittering particles.

Observation and Test.	Conclusion.
(1) Metallic particles without incrustation.	
(a) Color: yellow, white, red	Au, Ag, Cu.
(2) *Malleable* beads with incrustation.	
(a) Faint yellow incrustation, hot; white, cold.	Sn.
(b) Yellow incrustation, hot and cold	Pb.
(3) *Brittle* beads with incrustation.	
(a) Yellow incrustation, hot and cold	Bi.
(b) White incrustation, white fumes	Sb.
(4) Magnetic particles	Fe, Ni, Co.
(5) Garlic-like odor	As.
(6) Reddish incrustation, no bead	Cd.

3. Heat the substance on charcoal before the *blow-pipe flame* without the addition of sodium carbonate.

Observation and Test.	Conclusion.
(1) The mass fuses, is absorbed by the charcoal.	Alkali metal salts.
(2) An infusible white mass is formed.	
(a) Litmus, alkaline	Alkaline earths.
(b) Heated with $Co(NO_3)_2$, blue	Alumina (silica, phosphates).
(c) Heated with $Co(NO_3)_2$, green	Zinc oxide.
(d) Heated with $Co(NO_3)_2$, violet	Magnesia.
(3) Lively combustion of charcoal	Chlorates, nitrates.
(4) Incrustations, etc., as in § 2	

4. Heat a coarse grain or two of the substance in the *metaphosphate bead* in the oxidizing flame of the bunsen burner.

Observation.	Conclusion.
(1) "Skeleton" in the bead.	
(a) Colorless "skeleton"; heated with a trace of ferric oxide gives ferric bead.	Silica.
(b) Heated with ferric oxide, colorless.	Tin.
(c) Metallic particles	Gold or platinum.
(2) The bead is colored, when hot (h.) or cold (c).	
(a) Blue (h), blue (c)	Cobalt.
(b) Green (h), blue (c)	Copper.
(c) Green (h), green (c)	Chromium.
(d) Brown-red (h), light yellow to colorless (c); red (reducing flame) (h), greenish (c).	Iron.
(e) Reddish brown (h), yellow or colorless (c).	Nickel.[1]
(f) Yellowish brown (h), light yellow or colorless (c).	Bismuth.
(g) Violet (h), amethyst (c)	Manganese.

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[1] A borax bead gives a better test for nickel: brown (c).

5. Moisten the substance with hydrochloric acid and test its behavior on a platinum wire in the *flame*. In case of doubt, match the flame color with that produced by a known sample of the suspected substance held on a second wire next to the unknown.

Observation.	Conclusion.
(1) Intense yellow, persisting	Na.
(2) Violet to bluish	K, As, Pb, Sb.
(3) Crimson	Sr (Li).
(4) Brick-red	Ca.
(5) Green	Ba, Mn, H_3BO_3.
(6) Intense blue-green	Cu.

6. Warm a *little* of the substance with concentrated sulphuric acid in a test-tube. *Very little* should be tried first, as chlorates produce explosions.

Observation and Test.	Conclusion.
(1) Colorless gas:	
(a) Drop of lime water, cloud	CO_2, carbonates, organic acids.
(b) Acid blackened	*Organic matter.*
(c) Inflammable, blue flame	CO, oxalates, formates, cyanides.
(d) H_2S odor	Sulphides.
(e) SO_2 odor	Sulphites.
(f) Fumes with NH_3; cloud with drop silver nitrate solution.	Chlorides.[1]
(g) Etches glass	Fluorides.
(2) Brown gas:	
(a) Br odor	Bromides.
(b) NO_2 odor	Nitrates, nitrites.
(3) Violet gas:	
Black sublimate	Iodides.
(4) Yellow gas:	
(a) Non-explosive	Chlorine, from hypochlorites.
(b) Explosive	Chlorates.

II. *The Substance is a Metallic Solid.*

1. The blow-pipe test, without sodium carbonate, in the reducing flame is tried, as described above, I, 3. Consult also I, 2.

2. The substance is heated in a sealed glass tube: a sublimate of Hg, As or Cd may be obtained.

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[1] $HgCl_2$, HgCl, AgCl, $PbCl_2$, do not evolve HCl readily.

3. A small portion is warmed with water slightly acidified with acetic acid. An evolution of hydrogen indicates a light metal (alkali or alkaline earth metal; or manganese).

III. *The Substance is a Liquid.*

1. Evaporate a portion of the liquid to see if a solid residue is left. Such a residue is tested according to I. If no residue is left only volatile substances (ammonia, volatile acids, ammonium carbonate, arsenic chloride, mercuric chloride, etc.), can be present in solution.

2. Test the solution with litmus paper.

(*a*) If it is *neutral,* it is ready for analysis according to the systematic wet analysis in Part C (p. 68), for metal ions, and Part D, (p. 77) for acid ions.

(*b*) If it is *acid,* a free acid is present or a hydrolyzed salt of a weak base and a stronger acid. It is also ready for analysis according to Part C (p. 68) and Part D (p. 77).

(*c*) If it is *alkaline* a free alkali or alkaline earth is present or a hydrolyzed salt of one of these bases with a weak acid. Hydrochloric acid is added in excess to it and the mixture warmed[1]:

(1) *No precipitate* is formed. The acidified solution is ready for analysis according to Part C, p. 68.

(2) A *precipitate is formed and redissolved* in the excess of acid (*e.g.* recall the behavior of aluminates, stannates and similar salts); the acid solution is analyzed according to Part C, p. 68. The evolution of hydrogen sulphide indicates the presence of a sulphur acid salt (*e.g.*, sulph-arsenite, etc.), of hydrocyanic acid that of complex cyanogen salts.

(3) A *precipitate is formed and not re-dissolved.* The *acid solution* is filtered and analyzed according to Part C, p. 68. The *precipitate* is treated as a *new unknown* and brought into solution according to Part B, p. 66, or, if it cannot be dissolved, it is treated as an "Insoluble" according to Part E, p. 81. (See the previous § (2) in regard to the significance of any evolution of a gas.)[2]

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[1] See Part D, p. 77, in regard to the analysis for acid ions.

[2] If hydrocyanic acid is evolved and a precipitate is formed, the precipitate should be examined according to Fresenius, p. 529.

B. THE SOLUTION OF SUBSTANCES.

I. *The Substance is a Non-Metallic Solid.*

Try to dissolve the substance by using the solvents in the order: water, dilute hydrochloric acid, dilute nitric acid, concentrated hydrochloric acid, concentrated nitric acid, aqua regia (3 volumes concentrated nitric and 1 volume concentrated hydrochloric acid), each first cold, then hot. A very small amount of the material is tested with the solvents in the order given, and when the proper solvent is ascertained a larger quantity (about one gram) is brought into solution for the wet analysis. If a substance dissolves with difficulty in an agent, its behavior towards the subsequent ones is ascertained before the solvent is chosen.

All changes, such as effervescence (CO_2,H_2S, NO_2,H_2, etc.), the separation of sulphur, etc., should be noted.

1. *The substance is completely soluble in water.* Test the reaction of the solution with litmus; if it is *neutral* or *acid* it is ready for analysis according to Part C, p. 68; if it is *alkaline*, work according to the instructions given in III, 2 (*c*), p. 65.

2. *The substance is not completely soluble in water.* Filter a portion of the liquid and evaporate it in a clean dish: if more than a trace remains, the solution is treated according to the preceding paragraph 1. The undissolved portion is treated according to the next paragraph 3. Frequently it is permissible to mix the aqueous solution obtained with an acid solution of the remainder of the material as obtained in 3, and to make only one analysis. But such a step must be expressly stated in a report. For certain purposes, such as soil, fertilizer and some mineral analyses, separate analyses of water soluble, acid soluble and acid insoluble components are required.

3. *The substance is soluble in acid.* If dilute hydrochloric or nitric acid has been used, proceed with the analysis of the solution according to part C, p. 68. But, if conc. nitric acid or aqua regia has been used, it is best to remove most of the excess of acid by evaporation in a porcelain dish on the steam bath before going on to Part C, as otherwise difficulties will be met when hydrogen sulphide is used. If concentrated hydrochloric acid has been used, the solution must be diluted first with two or three

volumes of water: a precipitate may be silver, lead or mercurous chlorides, which are more or less soluble in concentrated hydrochloric acid, most likely as complex salts which are decomposed by water. If such a precipitate is formed, it is best to try dilute nitric acid as a solvent — it may often prove much better. The excess of hydrochloric acid is best evaporated only *after* a *first* treatment of the diluted solution with hydrogen sulphide in its proper place (p. 68), to precipitate arsenic and mercury, whose chlorides are volatile. For a complete precipitation of the other sulphides (lead, cadmium, etc., it is best to evaporate then the excess of acid (*cf.* p. 25, 1*b*).

4. *The substance is completely or partly insoluble* in the above acids. Any such part is treated as an "insoluble substance" according to Part E (see p. 81).

II. *The Substance is a Metal or Alloy.*

A little of the substance is tested according to 1 and 2, and a larger amount (one-half to one gram) used for the actual analysis.

1. A little of the *metal* or *alloy* is treated with *dilute nitric* acid. If a crystalline salt separates, some water is added.

(*a*) If a clear solution results, about a gram is dissolved in the same way and after removal of the excess of nitric acid the solution is treated according to Part C (p. 68).

(*b*) A *dark* residue is left. This indicates the presence of gold, platinum or graphite. The residue is collected, and if it is metallic, it is dissolved in *aqua regia* and the solution tested for *gold* and *platinum* (p. 70, § 3, and p. 71, § 5) after evaporation of the *aqua regia*.

(*c*) A pure *white solid* is left. This consists usually of stannic or antimonic oxides which may retain other metal oxides. It is best to discard the solution and the precipitate,[1] and to proceed according to 2.

2. A little of the *metal* or *alloy* is treated with *aqua regia* (3 volumes concentrated hydrochloric and 1 volume concentrated nitric acid). A *white residue* may contain lead or silver chlorides. The *solution* is decanted and, after the evaporation of most of the *aqua regia*, analyzed according to Part C, II (p. 68); the *residue* is washed with some water and tested for *silver* and *lead* according to I, p. 68.

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[1] An alternative method is given in Fresenius, p. 443.

C. THE ANALYSIS FOR METAL IONS OF SUBSTANCES SOLUBLE IN WATER, ACIDS OR AQUA REGIA.

I. THE PRECIPITATION OF THE SILVER DIVISION OF THE COPPER GROUP.

1. *The solution*[1] *is treated with a small excess of hydrochloric acid,* unless it already contains this acid. A *precipitate* is collected on a filter, washed and examined for *lead, silver* and *mercurous chlorides* according to p. 31. The *filtrate,* including the washings, or a solution in which hydrochloric acid gives *no precipitate,* is treated according to II, which follows:

II. THE PRECIPITATION OF THE ARSENIC GROUP AND OF THE COPPER DIVISION OF THE COPPER GROUP.

1. *Hydrogen sulphide* is passed into the cold solution to saturation, a precipitate is collected on a filter and washed with a little water. Hydrogen sulphide is then passed into the *heated* filtrate, whether a precipitate has been formed or not, to insure the precipitation of arsenic (see p. 36, 2). If a precipitate is formed, it is added to the first precipitate, the mixture being cooled before it is filtered. The filtrate or in case no precipitate was obtained, the clear liquid is diluted with four or five volumes of water and treated in the cold with hydrogen sulphide to insure the complete precipitation of metals (Cd, Pb, etc.), whose sulphides often are not precipitated in the presence of much free acid (see pp. 25 and 32). For very exact work it is best even to remove almost all of the excess of acid by *evaporation* at this point, the residue left by evaporation being dissolved in water and as little hydrochloric acid as possible and the solution treated again with hydrogen sulphide *in the cold. All the sulphides,* **S**, are collected on a filter and washed with water. The final filtrate (**F**) or the solution in which hydrogen sulphide gave no precipitate is reserved for analysis according to V, p. 72.

2. *A small portion of the precipitated sulphides* is tested to see whether both the *copper* and the *arsenic groups* or only one is present: it is warmed with a little light-yellow ammonium sulphide. We distinguish three cases.

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[1] Prepared according to III, p. 65, if the original substance is a liquid; according to I, p. 66, or II, p. 67, if it is a solid.

(*a*) *Complete solution* insures the *absence* of the *copper group* (see, however, p. 26, as to the loss of a trace of *copper*, which can be found by reprecipitation of the sulphides by hydrochloric acid and resolution of the arsenic group in sodium sulphydrate, in place of ammonium sulphide, the trace of copper sulphide being left undissolved). If the copper group is *absent*, the whole of the sulphide precipitate S is analyzed according to IV below for the *arsenic group* of metals.

(*b*) *A colored residue* is left. The *copper group* is *present*. The solution is filtered from this colored residue, and hydrochloric acid in excess is added to the filtrate: a pure white precipitate is *sulphur* from the ammonium sulphide (treat a few drops of light-yellow ammonium sulphide with water and hydrochloric acid for a comparison). Benzene may be added to the mixture; if only a *whitish residue* is left, the *arsenic group is absent* and the whole mass of the precipitated sulphides, S, is examined only for the metals of the *copper group* according to III below.

(*c*) *A colored residue* is left and hydrochloric acid gives with the *ammonium sulphide filtrate a colored precipitate. Both the arsenic and the copper groups* are present. The whole quantity of the precipitated sulphides S is extracted twice with darker yellow ammonium sulphide (to insure the *complete* solution of stannous and antimonous sulphides), the *residue* is analyzed for the *copper group* metals according to III below; the filtrate is acidified with hydrochloric acid, the sulphides of the *arsenic group* brought on a filter and analyzed according to IV.

III. The Analysis of the Copper Group.

Test the precipitate for *mercury*, *lead*, *bismuth*, *copper* and *cadmium* according to the analysis of the "Copper Division," p. 32, § 4.

IV. The Analysis of the Arsenic Group.[1]

1. The *sulphides* of the *arsenic group* obtained according to II 2 (*a*), above, or II 2 (*c*), above, are freed, as far as possible, on the filter from adhering water by suction over the filter pump. They are heated in a test-tube with exactly 10 *c.c.* concentrated *hydrochloric acid* (*sp. gr.* 1.2, *side-shelf*), the mixture is brought

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[1] A. A. Noyes and Bray, Technology Quarterly, September, 1906.

almost to boiling by immersion in a beaker full of boiling water for 10 minutes. 5 c.c. water are added to the solution, the latter is filtered, and the residue **R** washed once with 5 c.c. water, which is separated from the filtrate, **F**. The filtrate **F**, containing any antimony and tin which may have been present, is diluted with 30 c.c. more of water and reserved for analysis according to § 6. The residue **R**, which may contain arsenic, gold and platinum (and sulphur), is washed with dilute hydrochloric acid to remove the last traces of antimony and tin, and then analyzed according to § 2.

2. If *gold* and *platinum* are to be considered, the residue **R** is analyzed according to § 3; if they are not to be considered, it is tested only for *arsenic* according to p. 36, 3 (*c*) or 4 (*b*) (molybdate test or cyanide test).

3. If *gold* and *platinum* as well as *arsenic* are to be considered, the residue **R** obtained in § 1 is warmed in a porcelain dish with 5–10 c.c. dilute hydrochloric acid and solid potassium chlorate added in *small portions* until the oxidation of the sulphides is complete. Any sulphur is filtered off and the solution (**S**) concentrated to about 2 c.c. If the solution is yellow or if a yellow precipitate (K_2PtCl_6) has formed, *platinum* is indicated. If it is colorless proceed to § 4; if it is yellow, the 2 c.c. solution is further concentrated until potassium chloride crystals appear, then the yellow *potassium chloroplatinate* is collected on a very small filter and washed with a cold saturated potassium chloride solution. The filtrate is reserved for § 4. (Why is K_2PtCl_6 less soluble in KCl solution than in water?) The precipitate is dissolved in a few c.c. hot water and treated with a few drops of potassium iodide solution; a deep-red solution, K_2PtI_6, or black precipitate PtI_4 confirms *platinum.*

4. The filtrate from the potassium chloroplatinate or the *colorless solution* **S** obtained in § 3, is rendered alkaline (test) with ammonia, the cooled solution is filtered, if necessary, any precipitate (antimony or stannic hydroxides) being rejected, a cubic centimeter of magnesium nitrate mixture and one-third volume clear concentrated ammonia is added to the clear filtrate to precipitate magnesium ammonium *arsenate.* If no precipitate forms immediately, rub the walls of the test-tube gently with a glass rod for a minute or two, as crystallization is often delayed.

A precipitate shows the presence of *arsenic*. If there is no precipitate proceed to § 5. A precipitate is collected on a very small filter, washed once with concentrated ammonia, the filtrate F′ being reserved for *gold* tests given in § 5, and the *arsenate* precipitate dissolved in a little dilute nitric acid. A portion of this solution, boiled with four or five volumes of molybdate solution, should give a yellow precipitate of ammonium *arseno*-molybdate, confirming *arsenic;* a second portion, treated with silver nitrate, filtered from any precipitated silver chloride and covered with a layer of dilute ammonia should show a brown ring of silver *arsenate.*

5. The filtrate F′ separated from the magnesium ammonium arsenate in § 4 or the solution in which magnesium nitrate mixture failed to precipitate any arsenic, is treated with two to 3 c.c. saturated oxalic acid solution, and the mixture evaporated to 3–4 c.c. to expel the excess of ammonia. The residue is made slightly acid with oxalic acid, diluted to 15 c.c. and heated on a steam bath for several minutes. A purple precipitate shows *gold.*

6. The filtrate F of § 1 remains to be tested for *antimony* and *tin.* The tests may be carried out as on p. 40, 2, by the method of reduction with a steel nail or with tin and platinum. In testing for tin with mercuric chloride, the acid solution must be considerably diluted, as mercurous chloride is soluble in strong hydrochloric acid.

The following method may be used instead:

(*a*) The filtrate F as obtained in § 1 is heated in a test-tube placed in a beaker of hot water (90 degrees) and treated with hydrogen sulphide gas for five minutes. If no precipitate (*antimony* sulphide) forms, add 5 c.c. water and treat again with hydrogen sulphide at 90 degrees. An orange-red precipitate indicates *antimony.* (In the cold tin sulphide could be precipitated.) Five c.c. water should be added once more and the treatment repeated to insure complete precipitation of the *antimony.* The filtrate or the solution in which no precipitate was formed is examined for *tin* according to (*c*), the precipitate of antimony sulphide examined according to (*b*):

(*b*) The sulphide precipitate obtained in (*a*) is dissolved in very little concentrated hydrochloric acid, the solution evaporated to

1 c.c. and then treated with some pure tin placed on platinum foil; a black deposit on the platinum indicates *antimony*. It is washed well with water and then treated with some sodium hypobromite (1 to 2 c.c. bromine water added to 2 c.c. sodium hydroxide solution). *Antimony* does not dissolve, arsenic (if present) would dissolve.

(*c*) The filtrate from the antimony sulphide, § (*a*), is examined for *tin* as follows: a portion is diluted with water and treated with hydrogen sulphide in the cold: a yellow precipitate (tin sulphide) indicates *tin*. A second portion is boiled to remove hydrogen sulphide and then treated with an iron nail for ten minutes and the solution then tested with mercuric chloride: a white precipitate of mercurous chloride or a gray one of mercury proves *tin*.

V. THE IRON GROUPS (*and possibly the Alkaline Earths as Phosphates, Borates, Fluorides, Oxalates, etc.*).

To appreciate the requirements for a correct course of analysis of the solution remaining after the removal of the silver, copper and arsenic groups the student must consider in particular the two following points:

1. He must first recall the fact that tartrates, citrates, sugar, etc., interfere with the precipitation of hydroxides, phosphates, etc., of metals of these groups (p. 59), and since aluminium and chromium are to be precipitated as hydroxides, the alkaline earths as phosphates or carbonates, organic matter of the above nature, if present, must be *destroyed* before the further analysis is made. All these organic compounds char on being heated (p. 62, 3). A small portion of the original unknown is tested in this way for organic matter if the test has not been made before this (p. 60).

(*a*) If *organic* compounds *are present* and particularly if the odor of burnt sugar (sugar, tartrates) is developed when the original unknown is heated in a glass-tube (p. 62), the organic matter must be destroyed before the analysis for the iron and alkaline earth groups is continued: about one-fourth of the solution which is to be examined for these groups is reserved for the examination for sodium and potassium according to VII 3, (p. 76). The remainder of the solution is evaporated in a platinum dish (Instructor), an equal part of dry sodium carbonate and a little potassium nitrate are mixed with the dried residue and the

mixture is gently heated until the organic matter is destroyed. The mass is extracted with hydrochloric acid in excess and analyzed according to § 3, p. 72 (but first read § 2).

(*b*) In the *absence of organic matter* proceed to § 3, p. 72, after reading § 2.

2. The *second complication* that the student must consider is the fact that whereas ammonium hydroxide and sulphide in the presence of ammonium chloride will not precipitate a *sulphide* or *hydroxide* of the alkaline earths — as these are sufficiently soluble — they may under certain conditions precipitate *insoluble salts* (e.g., *phosphates, fluorides, oxalates,* etc.) of the *alkaline earths.* These would then be mixed with the hydroxides and sulphides of the iron group metals and, unless they were considered, they might be entirely overlooked. For instance, if the original unknown contained barium phosphate, hydrochloric acid would have been used as solvent. When ammonium chloride and ammonia are added to the solution for the precipitation of the iron groups, the barium phosphate would be reprecipitated, according to:

$$\underline{Ba_3(PO_4)_2} + 6\,HCl \rightarrow 3\,BaCl_2 + 2\,H_3PO_4 \qquad (1)$$

$$3\,BaCl_2 + 2\,H_3PO_4 + 6\,NH_4OH \rightarrow \qquad (2)$$

$$3\,BaCl_2 + 2\,(NH_4)_3PO_4 + 6\,H_2O \rightarrow \qquad (3)$$

$$\underline{Ba_3(PO_4)_2} + 6\,NH_4Cl + 6\,H_2O$$

(Why should *ammonium phosphate* precipitate the barium phosphate (equation (3)), when phosphoric acid does not (equation (1))? To what is the difference in the precipitating power of the two due?) Considering (1), (2), (3), it is evident that *this complication* will only be *possible* when the *original solution* (e.g. (1)) is not neutral (usually only when it is *acid*; when it is alkaline, only in the presence of organic matter), *and* when *ammonia precipitates a solid* even *before* the addition of *ammonium sulphide.* If both of these conditions are fulfilled, alkaline earths *may* come down in the iron group, otherwise not. An acid solution and precipitation by ammonia may, however, be due to the presence also of *other* metal salts, as in the case of ferric chloride or nickel phosphate, etc.

3. The PROCESS OF ANALYSIS based on the above considerations is the following: In the absence of organic matter, [or after its

removal, if present (see 1 (*a*), p. 72)], boil a *small portion* of the solution which has been freed from the arsenic, copper and silver groups, to remove hydrogen sulphide, and add to this or to the original solution, if these are absent, a few drops of bromine water (to convert ferrous into ferric iron), and boil the solution to remove the excess of bromine. Cool the solution, add 4 or 5 c.c. *ammonium chloride* solution and enough *ammonia* to make the reaction of the solution *alkaline* to litmus. We distinguish three cases :

(*a*) If *no* precipitate is formed, *aluminium, chromium* and *iron* are *absent,* as well as the *phosphates, borates,* etc., of *alkaline earths.* Add *ammonium sulphide* to the solution. A precipitate may contain only *nickel, cobalt, manganese* and *zinc.* If a sulphide is precipitated the whole of the main solution is treated with ammonium chloride, ammonium hydroxide and ammonium sulphide and the *precipitate* is analyzed only for these four metals according to p. 22, 3 and II, and p. 24, IV. The *filtrate* from the sulphides or the solution in which ammonium sulphide gave no precipitate is *reserved* for analysis according to VI and VII (p. 76) for the alkaline earths and alkalies.

(*b*) *Ammonia* gives a precipitate, but the original solution of the unknown was *neutral.* In this case the phosphates, etc., of the alkaline earths are again absent. Proceed again as in (*a*), but make a complete analysis of the IRON GROUPS (p. 21).

(*c*) *Ammonia gives a precipitate* and the original solution of the unknown was *not neutral.* Treat the whole of the main solution with ammonia, and an excess of ammonium sulphide and heat the mixture. The *filtrate* is reserved for analysis according to VI and VII (p. 76), for the alkaline earths and alkalies. (See, however, p. 22, 2, Analysis of Iron Groups, in regard to the *detection of a trace of nickel* in a *brown* filtrate). The *precipitate* may contain *all the metals* of the *iron group* as well as *barium, strontium, calcium* and *magnesium* (as phosphates, etc.). It is treated, according to its bulk, with 50 to 150 c.c. dilute hydrochloric acid (1 part dilute acid, sp. g. 1.12, and 3 parts of water), which is allowed to act for five minutes. A residue **R** and the filtrate **F** are analyzed as follows:

(1). A *black residue* **R** is brought on a filter and examined for *nickel* and *cobalt* according to p. 22, II.

(2). A *small portion* of the filtrate F is treated with a few drops of sulphuric acid, as long as a precipitate forms. An *immediate precipitate* proves *barium*, a more slowly formed precipitate is probably *strontium* sulphate. It is collected, washed, and examined with the flame for these metals (p. 82, 4). The *filtrate from the sulphates* or, if no sulphate was precipitated, the solution to which sulphuric acid was added, is treated with four volumes of alcohol, to precipitate *calcium* sulphate. If a precipitate is obtained, it is brought on a filter, washed with alcohol, shaken with a little water, and an excess of ammonium oxalate added to the solution: an immediate precipitate confirms the presence of *calcium*. Without this confirmation calcium must not be reported.

(3). The larger portion of the filtrate F is heated to remove hydrogen sulphide, and treated with an excess of bromine water, to convert any ferrous into ferric salt; the excess of bromine is removed, and a little of this solution (S) tested with ammonium thiocyanate for *iron*. If iron is found, its original form, as *ferrous* or *ferric* iron or both, is determined by examining the original unknown.

(4). Irrespective of the presence or absence of iron, ferric chloride[1] is added to the main part of the solution (S) (obtained in (3)) until a drop of the mixture when tested with ammonia gives a *reddish* precipitate. Then sodium carbonate is added until a slight permanent precipitate is formed. This is redissolved *in as little hydrochloric acid* as possible and aluminium, chromium and iron are precipitated with barium carbonate according to III, § 2, p. 23. The precipitate is tested for *aluminium* and *chromium* according to § 3 (*a*) or 3 (*b*), p. 24. Use the filtrate for (5).

(5) Precipitate *manganese* and *zinc* sulphides from the filtrate

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[1] Ferric chloride is added to separate phosphoric acid from magnesium (Lecture), which may be present. The acid solution S could contain magnesium chloride, ammonium chloride and phosphoric acid, if magnesium and phosphate ions were in the original solution of the unknown. After the addition of an excess of ferric chloride, when the solution is neutralized, ferric phosphate is precipitated: $MgCl_2 + NH_4Cl + FeCl_3 + Na_3PO_4 \rightarrow MgCl_2 + NH_4Cl + \underline{FePO_4} + 3\,NaCl$. Magnesium chloride is in solution. Why is ferric phosphate precipitated in preference to magnesium ammonium phosphate? Precipitate some ferric phosphate and some magnesium ammonium phosphate separately and add acetic acid to each. Does the experiment confirm your conclusion?

of (4) as described in IV, p. 24, test a *precipitate* for these metals, and reserve the *filtrate* for the following:

(6) The filtrate from the manganese and zinc sulphides or the solution in which they were found to be absent must still be examined for *magnesium*. It is heated to boiling, treated with sulphuric acid as long as barium sulphate is formed, if this has not already been done; without filtration ammonia and ammonium oxalate and ammonium carbonate are added to remove calcium and strontium. The solution is filtered from these precipitates, the filtrate is concentrated and tested for *magnesium* with ammonia and sodium phosphate. Magnesium can be confirmed eventually by the spectroscope, p. 6, § 10.

VI. THE ALKALINE EARTHS.

The solution from which the silver, arsenic, copper and iron groups and any organic acids (see V, 1 (*a*), p. 72) have been removed, is examined according to p. 9, for *barium, strontium, calcium,* and *magnesium,* regard being taken of the possible presence of traces. Ammonium phosphate is used for the detection and removal of *magnesium,* and the filtrate from it is analyzed for sodium and potassium according to the next paragraph, VII, 2 (below).

VII. THE ALKALIES.

1. The original unknown is tested for *ammonium* according to p. 1, 2 (*a*).

2. In the absence of organic substances, the solution obtained in VI is evaporated to dryness, the ammonium salts removed *completely* by gentle ignition of the solids, and any residue is dissolved in as *little* water as possible and tested for *sodium* and *potassium* according to p. 2, 5 (*a*) and 4 (*a*) and (*b*). An iodide gives a red solution with chloroplatinic acid. It is best to remove hydriodic acid by evaporation with nitric or concentrated hydrochloric acid, in such a case, and then to make the test.

3. In the presence of *organic* matter, the solution reserved in V, 1 (*a*), p. 72, for the determination of the alkalies, is evaporated to dryness in a porcelain dish. The residue is carefully moistened with pure concentrated sulphuric acid and the mixture gently heated until most of the acid is expelled. The residue is extracted with water, the solution heated, and the metals of the iron groups

precipitated by means of ammonium chloride, ammonia and ammonium sulphide, the alkaline earths by means of ammonium carbonate and ammonium phosphate, and the filtrate from the mixed precipitate analyzed according to VII, 2.

D. THE ANALYSIS FOR THE ACID IONS OF SUBSTANCES SOLUBLE IN WATER, ACIDS, OR AQUA REGIA.

Introductory. — The acid tests used are especially those that are carried out in *acid* solutions, since metals, other than the alkalies, are likely to interfere with tests made in neutral or alkaline solutions. Such metals may, however, be removed, as a rule, if desired, and the acids obtained in the form of *sodium salts,* by treatment of the compound to be analyzed with sodium carbonate. To accomplish this, compounds soluble in water are boiled with sodium carbonate solution, compounds insoluble in water are fused with sodium carbonate. When organic acids are to be converted into sodium salts, the compound is boiled with sodium carbonate, irrespective of its solubility in water or acid.

As practically all the most important tests for the acid ions are made in acid solution, the treatment with sodium carbonate is, except in rare cases, unnecessary and may be avoided.

If the substance is insoluble in water or acids (p. 67, B, I, 4), *it is analyzed according to Part E, p.* 81.

Alkaline solutions should be acidified and any precipitate, insoluble in excess of acid, as well as the acid solution obtained treated as new unknowns.

The metals having been determined, the solubility of unknowns in water or acid will usually serve to shorten the course of analysis for the acids very considerably. *The Table of Solubilities on p.* 88 *should be consulted.* The results of the *Preliminary Examination,* especially of I, 6, p. 64, will also be very helpful.

Carbonic, arsenious, arsenic, chromic and *hydrosulphuric* acids, and usually *silicic* acid, if they are present, should have revealed themselves in the course of the analysis for metal ions. Similarly, amphoteric substances, such as aluminium hydroxide (p. 11), zinc, lead hydroxides, stannic acid, antimonic acid, etc., will have been found in the analysis for metal ions: the decision as to the rôle of such amphoteric compounds in the original substance is based on the complete analysis and the observation of such properties as the neutrality, alkalinity, or acidity of the original solutions obtained, the common character of the compounds, etc. If the original solution of a salt of such an element in water reacts *acid*, it would indicate its presence as a *metal ion*, the amphoteric hydroxides forming weak bases whose salts with strong acids are partially hydrolyzed and give acid solutions. It may, however, contain the free acid itself (*e.g.* arsenic acid) or an acid salt. *Vice-versa*, an aqueous solution reacting *alkaline* would indicate that such an amphoter, if present, is present in the form of an alkali or alkaline earth salt of an *acid ion*.

I. The Hydrochloric Acid Group.

1. A small portion of a solid substance is dissolved in water and the solution *acidified with nitric acid* (any precipitate that is formed is filtered off and discarded); or, if the substance is insoluble in water, it is warmed gently with dilute nitric acid (if a residue is left it is removed by filtration and discarded[1]); or, if the unknown is a liquid, it is acidified with nitric acid. To the acid solution, thus obtained in any case, *silver nitrate* is added:

2. If *no precipitate* is formed, *all* the *acid ions* of the *hydrochloric acid group*, viz., chloride, bromide, iodide, hydrocyanide, thio-, ferro-, and ferricyanide and sulphide ions are *absent*:[2] Proceed to III, p. 78. As nitric acid might destroy the *sulphide ion*, its presence or absence, usually ascertained in the course of the analyses for metal ions, should be especially determined according to p. 52, 1 or 2.

3. If *silver nitrate* produces a *precipitate* in nitric acid solutions, one or more of the acid ions mentioned in 2 must be present. If a silver salt is precipitated, note its *color*, and test for the acid ions in the following order in small portions of the nitric acid solution prepared as in 1:

(*a*) *Thiocyanide* (white silver salt). — Test the solution with ferric chloride and ether (p. 16, 4 (*c*)).

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[1] But if the substance was originally found to be insoluble in *any acid* p. 67, B, I, 4), it is analyzed for metals and acids according to Part E, p. 81.

[2] It will be recalled that acid insoluble salts of these ions (e.g., AgCl, AgBr, AgCN, a number of ferro- and ferricyanides, etc, see table, p. 88) are analyzed according to Part E, p. 81.

(*b*) *Ferrocyanide* (white silver salt). — Test the solution with ferric chloride (p. 16, 4 (*a*)).

(*c*) *Ferricyanide* (red-brown silver salt). — Test the solution with ferrous sulphate (p. 18, 1 (*b*)).

(*d*) *Cyanide* (white silver salt). — Test the solution with ferrous sulphate and ferric chloride according to p. 52, 2 (*a*).

(*e*) *Sulphide* (black silver salt). — Test the substance according to p. 52, 1 or 2. H_2S is removed by ebullition. (*Vide,* Fresenius, p. 376, in regard to the cyanide test when H_2S is present.)

(*f*) *Iodide* (yellow silver salt). — Test the solution with sodium nitrite and starch solution or chloroform (p. 43, 4 (*a*) or 4 (*b*)).

(*g*) *Bromide* (pale-yellow silver salt). — Test the solution with chlorine water and chloroform, according to p. 43, 4 (*b*).

(*h*) *Chloride* (a white silver salt). — In the absence of cyanide, thio- and ferrocyanide ions, a white silver salt insoluble in nitric acid shows the presence of *chloride* ions. In the presence of bromides or iodides, test for *chlorides* according to p. 43, 5.

N.B. Cyanides, thio-, ferro- and ferricyanides interfere with these tests for iodides, bromides and chlorides. If the cyanide ions are present, proceed according to Fresenius, p. 376.

II. THE NITRATE AND PHOSPHATE GROUPS OF INORGANIC ACIDS.

Small portions of the original unknown are used for the tests for the remaining inorganic acids.[1] If the absence of any acid is proved by the solubility of the substance (Solubilities and comments, p. 88), the test for the acid is omitted.

1. *Chlorates.* — p. 54, 1 (*b*) and 3.
2. *Nitrates.* — p. 53, 2 (*a*). If chlorates, chromates, iodides or bromides are present, use the test, p. 52, 3, removing any

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[1] If no other metals than alkalies are present, a rather concentrated aqueous solution may be treated with *barium chloride* and rendered alkaline with ammonium hydroxide: the *absence of a precipitate shows the absence* of the *acids* given in II, 3–9, and III, 2–4; a *precipitate* shows the presence of one or more of these acids and the examination is made as above. Other metals than the alkalies may be removed by means of sodium carbonate as described on p. 77, carbonic acid removed from the solution by boiling it after it is acidified with nitric acid, and the barium chloride test for the phosphate group may then be applied. But with the precautions given, this group test may well be omitted, especially since the treatment with sodium carbonate frequently is not altogether satisfactory.

ammonia by boiling the alkaline solution before adding zinc and iron.

3. *Sulphates.* — Test the solution with barium chloride and hydrochloric acid or, in the presence of silver, lead or mercurous salts, with barium nitrate and nitric acid. Note the precautions given, p. 54, 1.

4. *Phosphates.* — Test a nitric acid solution of the unknown[1] with molybdanic acid according to p. 57, 2, using a considerable excess of molybdanic acid in the cold. Halogen acids, in large amount, interfere with the test and are best removed by evaporation with an excess of nitric acid.

5. *Borates.* — p. 56, 3 and 2. But if copper salts are present, the copper is removed by treatment with sodium carbonate (p. 77) before the green flame test is made. In cases of doubt, the flame test (p. 56, § 4) with examination of the spectrum will be most conclusive.

6. *Fluorides.* — p. 55, 2 or 1.

7. *Silicates.* — p. 55, 2 and 3 or 4.

8. *Carbonates.* — p. 55.

9. *Arsenites, arsenates, chromates* — are found in the analysis for metal ions.

III. Organic Acids.[2]

Organic acids should only be looked for if their presence is indicated by the preliminary tests, pp. 61–64. In doubtful cases the test given on p. 58 may be used in addition.

1. *Acetates* — test the unknown directly according to p. 58, 1.

2. *Oxalates* — treat a small amount of the unknown with warm dilute sulphuric acid (if a carbonate is present, the carbon dioxide is removed by boiling); cool the solution, and add manganese dioxide (free from carbonate): irrespective of the presence of a precipitate, effervescence of carbon dioxide (lime water test) proves the presence of *oxalates.*

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[1] Stannic phosphate is insoluble in nitric acid. If tin has been found, it is removed by precipitation with hydrogen sulphide in hydrochloric acid solution, the filtrate evaporated to dryness and a nitric acid solution of the residue tested as above.

[2] Only the acids on pp. 58 and 59 are considered. For tests for the innumerable other organic acids, Fresenius, Mulliken's "Identification of Organic Compounds" and similar works would have to be consulted.

3. *Salicylates* — p. 59.

4. To test for *tartrates*, all metals but the alkalies should be removed as far as possible (see, however, p. 58, in regard to aluminium and chromium). About one-half to one gram of a solid unknown or the proportionate amount of an unknown solution is freed from the heavier metal ions by means of hydrogen sulphide, ammonium sulphide and ammonium or sodium carbonate. The filtrate from the last precipitate obtained is rendered acid with hydrochloric acid and concentrated to a small bulk (20 c.c.), carbonic acid being removed by the same operation. The solution is then tested for tartrates according to p. 59, 3 (*a*), (*b*) and (*c*); it must respond to all three tests if tartrates are present.

E. THE ANALYSIS OF SUBSTANCES INSOLUBLE IN WATER, ACIDS, AND AQUA REGIA.

The most common and widely occurring substances of this kind are *silicates* and *silicon dioxide*. Related to these, are *stannic oxide*, *aluminium oxide* (native or ignited) and aluminates, *chromic oxide* (ignited) and *ferrous chromite* (chrome iron ore). There is also an insoluble modification of chromium chloride and one of chromium sulphate. The *sulphates* of *barium*, *strontium* and *calcium*, *calcium fluoride* (and other fluorides) are of rather common occurrence. Certain silver and lead salts, viz., *silver chloride*, *bromide*, *iodide* and cyanide, and *lead sulphate*, a number of ferro- and ferricyanides, etc., and *carbon* and *sulphur* complete the list of substances we are most liable to meet in this division. Although the lead and silver salts and fluorides are of less common occurrence than many of the other substances mentioned, the methods of analysis make it advisable to *remove* lead and silver salts, if they are present, and to have warning of the presence of fluorides, if they are present, before proceeding to the more common cases. The method of analysis given below is based on this idea. However, careful inspection of the substance and the application of the few preliminary tests given, if not made already, will as a rule enable one to shorten greatly the scheme of analysis and to go directly to the paragraphs whose instructions must be followed in a given case.

I. Preliminary Examination.

1. Examine the substance carefully: *carbon* (graphite, coal, etc.) and *sulphur* will usually reveal themselves by their color, *quartz* often by its appearance. *Carbon* may be confirmed by burning some of the substance on a platinum foil or on a porcelain crucible lid heated to bright redness. *Sulphur* may be confirmed by heating some of the substance in a small tube — a sublimate of sulphur will form — and by burning some.

2. Heat some of the pulverized substance with sodium carbonate in the reducing flame of the blow-pipe (see p. 62, 2): metallic beads will indicate the presence of *lead*, *silver* or *tin*. The presence of any or all of them can be most readily determined by analysis of the beads themselves: the metal or alloy is treated according to §§ 1 and 2, p. 67, and analyzed only for the three metals mentioned.

If *lead* is found, proceed, after completing the preliminary tests, with the *analysis* of the substance itself according to §1, p. 83, otherwise omit that paragraph; if *silver* is found, proceed similarly to § 2, otherwise omit it. If both have been found, proceed first to § 1 and then to § 2. The further course if *tin* is found, depends on the results of the remaining preliminary tests.

3. A small portion of the original unknown is tested with the metaphosphate bead (p. 63, 4) for *silicic* acid; another portion is fused in the loop of a platinum wire with sodium carbonate: effervescence indicates silicic acid. If *silicic* acid is found (and no lead or silver), proceed to § 3, p. 84, and make a test for fluorine and then proceed to § 4 and make a silicate analysis — in the absence of silicic acid omit the latter paragraph.

4. Heat some of the substance on a platinum wire in the reducing zone of the flame of the bunsen burner, cool it in the inside cone of the flame and then moisten the residue with a drop of hydrochloric acid: hydrogen sulphide will indicate a *sulphate* and the chlorides, heated in the edge of the flame will reveal *calcium*, *strontium* and *barium*, if present — often all three in succession, if they are all present. The rigorous analysis is made according to § 5, p. 86.

5. Test the substance for complex cyanides according to pp. 60–61, 1, (1) (*f*) and (*h*).

If they are found, proceed according to Fresenius, p. 529.

6. If the preliminary tests, 1 to 5, have failed to reveal any components, proceed to p. 86, § 3, and p. 86, § 5; or if after the removal of lead and silver, a residue remains which is not a silicate, proceed likewise with it to §§ 3 and 5.

II. Analysis.

1. *Examination and Removal of Lead Salts.* — If lead has been found or indicated in the preliminary test 2, heat about a gram of the substance with a concentrated, slightly acid (acetic acid) solution of ammonium acetate until all the lead (excepting possibly lead silicate) has been dissolved, reserve any insoluble residue for analysis according to §§ 2 to 5, and test the solution as follows:

(*a*) for *lead* by diluting a portion and adding an excess of sulphuric acid as well as by testing another portion with hydrogen sulphide (p. 28, *b*).

(*b*) for *sulphate* ions with barium chloride and hydrochloric acid.

(*c*) for *chloride* ions by diluting a portion and adding silver nitrate and nitric acid.

2. *Examination and Removal of Silver Salts.* — If silver has been found or indicated in the preliminary test 2, a portion of the unknown which has been freed from lead according to the preceding paragraph or has been found free from it, is used:

(*a*) It is warmed with a little potassium cyanide solution. Any undissolved part is reserved for analysis according to §§ 3–5. The solution is filtered, diluted and acidified with nitric acid (Care! hood! hydrocyanic acid fumes!). A precipitate (P) is collected, washed well, reduced on charcoal or by ignition with sodium carbonate in a porcelain crucible, and a metallic product tested for *silver*. The filtrate from the silver precipitate (P) is tested for *sulphates* by barium chloride.

(*b*) If silver has been found in (*a*) another portion of the lead free substance is treated in a porcelain dish with a piece of zinc and dilute sulphuric acid. When the silver salt is reduced, the acid solution is decanted and a portion tested for the *cyanide* ion according to p. 52, 2 (*a*). In the absence of cyanides the rest of the solution is tested according to p. 43, for *iodide* (4 *a*), *bromide* (4 *b*) and *chloride* (5) ions. If cyanogen is found the silver halides and cyanide are precipitated by silver nitrate and collected on a filter. The dry silver salts are fused in a porcelain crucible to decompose the cyanide, and the residue is fused again after the addition of sodium carbonate. The aqueous extract of the cooled mass is then tested for the halogens according to p. 43, as described above.

3. *Examination for Fluorine.* — A small amount of the substance freed from silver and lead or of the original substance, if these metals are absent, is fused with a little sodium carbonate in the loop of a platinum wire. The cooled mass is tested for *fluorides* according to p. 55, § 2, care being taken to add the sulphuric acid slowly to the mass on account of the carbon dioxide which is formed. If this test proves negative, test a little of the unknown directly for *fluorides*, according to p. 55, 2. Some fluorides (fluorspar) are scarcely decomposed by sodium carbonate, others are not decomposed by sulphuric acid. If fluorine is found, any tests for silicic acid according to § 4 must be carried out in platinum vessels.

4. *Analysis of Silicates*[1]. — If silicic acid is found by the preliminary examination (p. 82, § 3), proceed as follows:

(*a*) Lead and silver having been removed, if present, according to 1 and 2, and sulphur, if found, being removed by ignition in a porcelain crucible, about one gram of the finely pulverized silicate is mixed with two parts each of sodium and potassium carbonates and a little potassium nitrate. The mixture is fused in a small platinum dish. (Instructor. Read the precautions given in Fresenius, pp. 20 and 21, in regard to the proper use of platinum vessels.) The cooled mass is digested with water and then treated with hydrochloric acid in excess and the mixture evaporated to dryness on the steam-bath. The dry residue is dried an hour longer on the steam-bath or 10 minutes in an air bath at 120 degrees to render the silicic acid insoluble. The resi-

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[1] *Silicates which are decomposed by acids* are treated with an excess of hydrochloric acid, the mixture is evaporated to dryness and the silica rendered insoluble as in (*a*). The further analysis of the solution then obtained is carried out according to Part C, p. 68, for the metals. For the acid analysis, proceed as in (*b*) p. 85, excepting that the fusion is omitted.

due is then heated with water and hydrochloric acid, and the solution filtered from the *silica*. (Confirmative tests: p. 55.) The filtrate is analyzed for all the metals, excepting the alkalies,[1] according to the systematic method of analysis, Part C, p. 68.

(*b*) Another portion of the silicate is fused as above with sodium and potassium carbonate and a little potassium nitrate. The cooled mass is extracted with water, and the extract tested for the *acids* as follows:[2]

(1) A small portion is acidified with nitric acid, separated silica removed by filtration, and silver nitrate added to test for *chlorides*, *bromides*, etc. (see p. 78, I).

(2) Another portion is tested for *boric acid,* according to p. 56, 2 and 3.

(3) Another small portion is tested for *sulphates* (p. 54, 1).

(4) The main portion is acidified with nitric acid, the solution evaporated to dryness to render silica insoluble as described above. A portion of the dry residue (R) is extracted with hydrochloric acid and water, and tested for *arsenic* with hydrogen sulphide at 70 to 90 degrees. If arsenic is found (see p. 36), the whole of the dry residue is treated in the same way to remove the arsenic, and the filtrate from the arsenic sulphide is evaporated with nitric acid to dryness to remove the hydrochloric acid and the residue treated with water, nitric acid and molybdate solution for *phosphates* (p. 57, 2). If no arsenic is found, the main portion of the residue (R) is tested directly for *phosphates* (p. 57, 2).

(5) See 3, p. 84, in regard to the test for *fluorine*.

(*c*) The original silicate, if it was fused with alkali carbonates, must still be tested for the *alkalies*. One of the following three methods may be used :

(1) Mix the finely pulverized silicate with one part of pulverized ammonium chloride and eight parts of pure calcium carbonate, and heat the mixture in a covered platinum crucible to a moderate red heat for half an hour. The cooled mass is extracted with water, ammonium carbonate and ammonia are added to the filtered extract, and the filtrate from the precipitate is examined for the alkalies according to Part C, p. 76, VII, 2.

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[1] *Including the alkalies*, in the case of silicates decomposed by acids.

[2] In silicates decomposable by acids, the fusion is omitted.

(2) A little of the pulverized silicate is mixed with ammonium fluoride and the mixture gently heated in the Bunsen flame on the loop of a platinum wire. The mass is then extracted with a drop of water, and the flame test made for the alkalies with the aid of the spectroscope (see p. 2, 5 (*c*)).

(3) About half a gram of the pulverized silicate is heated in a platinum dish (Instructor) with a little water and with five c.c. each of hydrochloric and hydrofluoric acids. (Care! Work in a hood. The vapors injure the lungs and the skin!) When the silicate has dissolved, 5 c.c. dilute sulphuric acid is added, and the contents of the dish evaporated in the hood until heavy fumes of sulphuric acid are formed. The residue is extracted with water, all the metals excepting the alkalies removed by their group reagents and the alkalies tested for according to Part C, pp. 76, VII, 2.

5. *Examination for the Remaining Substances Enumerated* p. 81. — Silver and lead being absent or having been removed by ammonium acetate and potassium cyanide, according to 1 and 2, the substance is mixed with two parts each of sodium and potassium carbonates and a small amount of potassium nitrate, and the mixture fused in a small platinum dish. (Instructor.) The cooled mass is warmed with 50 c.c. of water, and the filtrate (F) analyzed according to *a* to *e*. The residue (R) is washed with more water until free from alkali carbonates, and then analyzed according to *f* for metal ions.

(*a*) Acidify about 25 c.c. of the filtrate (F) with hydrochloric acid, evaporate the solution to dryness, and dry the residue for one hour on the steam-bath, or ten minutes in an air-bath at 120 degrees, to render any silica insoluble. Heat the residue with water and hydrochloric acid. An insoluble residue would be *silicic acid* (see p. 55, 2, for a confirmative test). If a large amount of silica is found, the substance is a silicate and the analysis should be continued according to 4 (*a*), p. 84. A small amount of silica, which very frequently is found in minerals and ores, is removed by filtration, and the filtrate is tested according to (*b*) (below) for *lead, tin, aluminium, chromium* and *zinc*. (Why are these the only common metal ions besides the alkalies which can be present in this solution? In the form of what compounds are they obtained by the above fusion with alkali carbonates? If they

are found, does their presence at this place prove anything as to their occurrence in the original substance as basic or acid constituents?)

(*b*) (1) Test a portion of the solution for *lead* with dilute sulphuric acid.

(2) Add a steel nail to another portion of the solution and test the filtrate for *tin* with mercuric chloride (p. 37, 2).

(3) After removing any tin or lead by hydrogen sulphide, test the solution for *aluminium* by adding ammonium chloride and ammonia and boiling the mixture. (In the presence of chromium (see *e*), test any precipitate obtained by ammonia for aluminium according to III, 3, p. 24.)

(4) The solution freed from lead, tin and aluminium, according to (3) is tested for *zinc* with ammonium sulphide.

(*c*) Another portion of the filtrate (F) is acidified with hydrochloric acid and treated:

(1) With barium chloride for *sulphate* ions.

(2) With hydrogen sulphide, passed into the hot solution, for *arsenate* ions. A precipitate is tested for arsenic by means of potassium cyanide (p. 36, 4 *b*).

(*d*) Another small portion of (F) is acidified with nitric acid, and a part tested in the cold with molybdate solution for *phosphate* ions (p. 57, 2), and a second part with silver nitrate for *chlorides*.

(*e*) If the filtrate (F) is yellow, confirm the presence of *chromic acid* by means of lead acetate and acetic acid. (Does the presence of chromic acid here enable us to decide whether chromium was originally present with a valence of three or six?) (See p. 14, 1.)

(*f*) The residue (R) obtained under 5 contains the *bases* present in the insoluble unknown in the form of carbonates or oxides, excepting perhaps the bases which, owing to the amphoteric character of the metal hydroxides, were found, in part, at least, in 5 (*b*). The residue (R) is dissolved in dilute hydrochloric acid, and the acid solution analyzed according to the systematic method of analysis, Part C, p. 68.

SOLUBILITIES. * †

		Hydrogen.	Sodium.	Potassium.	Ammonium.	Magnesium.	Calcium.	Strontium.	Barium.	Aluminium.	Chromium.	Ferric.	Ferrous.
1	Oxide	....	w	w	....	A	W–A	W	W	A&I_9	A & I_{10}	A	A
2	Hydroxide	....	W	W	W	A	W–A	W	W	A	A	A	A
3	Chloride	W	W	W	W	W	W	W	W	W	W & I_{11}	W	W
4	Bromide	W	W	W	W	W	W	W	W	w	W & I	W	W
5	Iodide	W	W	W	W	W	W	W	W	w	w	w	W
6	Cyanide	W	W	W	w	w	W	W	W–A	....	a	....	a–i
7	Ferrocy	w	W	W	w	w	w	W	w–a	i	......	I	I
8	Ferricy	w	W	W	w	w	w	w	w	....	......	w	I
9	Sulphocy	w	W	W	W	w	w	W	w	W	w	w	w
10	Sulphide	W	W	W	W	a_4	W–A_6	W	W	a	a–i	a	A
11	Sulphate	W	W	W	W	W	W–I	I	I	W	W & I	W	W
12	Carbonate	W_1	W	W	W	A	A_7	A	A	....	a#	a#	A
13	Arsenite	....	W	W	w	a	a	a	a	....	......	a	a
14	Arsenate	w	W	W	w	a	a	a	a	a	a	a	a
15	Chromate	w	W	W	w	w	W–A	W–A	A	....	a	w	....
16	Phosphate	W	W	W	W	A_5	A_8	A	A	A	a	A	A
17	Borate	W	W	W	w	w–a	a	a	a	a	a	a	a
18	Fluoride	W	W	W	W	a–i	A–I	A–I	A–I	w	w	w	w–a
19	Silicate	I_2	W	W	....	a	a	a	a	A–I	a	a	a
20	Nitrate	W	W	W	W	W	W	W	w	W	W	W	W
21	Chlorate	w	W	W	W	w	w	W	w	w	w	w	....
22	Acetate	W	W	W	W	W	W	W	W	W	w	W	W
23	Oxalate	W	W	W	W	a	A	a	a	a	w–a	a	a
24	Tartrate	W	W	W_3	W_1	w–a	a	a	a	w	w	W	w–a
25	Citrate	W	W	W	W	w	w–a	a	a	w	w	W	w

* *W* Soluble in water.
A Soluble in acid (hydrochloric or nitric acid or aqua regia).
W-A Somewhat soluble in water, soluble in acids.
W-I Somewhat soluble in water, scarcely more soluble in acids.
A-I Difficultly soluble in acids.
I Insoluble in water and acids.
Small letters are used for less common salts.

† See the *comments* on p. 90.

‡ Basic salts.

SOLUBILITIES.*

Cobalt.	Nickel.	Zinc.	Manganese.	Silver.	Lead.	Mercurous.	Mercuric.	Cupric$_{13}$.	Bismuth.	Cadmium.	Arsenious.	Stannous.	Stannic.	Antimonous.	
A	A	A	A	A	A	A	A	A	A	A	A	A	A &I	A	1
A	A	A	A	....	A	....	....	A	A	A	....	A	A	A	2
W	W	W	W	I	W–I	A–I	W	W	W–A$_{13}$	W	W–A	W	W	W–A$_{17}$	3
W	W	W	W	I	W–I	A–1	W	W	w–a	W	W–A	w	w–a	w–a	4
W	W	W	W	I	W–I	A	A	W	a	W	w–a	W	w	w–a	5
a–i	a–i	A	a	I	a	....	W	a	......	a	....	....	....	......	6
I	I	A–I	a	I	a	....	....	I	i	a–i	....	i	i	......	7
I	I	A	I	I	w–a	....	i	....	i	a–i	....	i	....	......	8
w	w	w	w	I	a	A	W	a	......	w–a	....	....	w	......	9
A	A	A	A	A	A	A	A$_{12}$	A	A	A	A	A	A	A	10
W	W	W	W	W–A	A–I	W–A	W	W	w	W	....	W	....	......	11
A	A	A	A	A	A	a	a	A	A	A	....	....	....	......	12
a	a	a	a	A	A	a	a	A	......	....	....	....	....	a	13
a	a	a	a	a	A	a	a	a	a	a	....	....	....	a	14
a	a	w	w	a	A–I	a	w–a	w	a	a	....	a	....	a	15
A	A	A	A	a	A	a	a	A	a	a	....	a	A	w–a	16
a	a	a	a	a	a	....	....	a	a	w–a	....	a	....	......	17
w–a	w–a	w–a	a	w	a	w	w–a	a	w	w–a	....	w	w	w	18
a	a	a	a	....	a	....	....	a	......	a	....	....	....	......	19
W	W	W	W	W	W	W	W	W	W–A$_{16}$	W	....	....	....	.....	20
W	W	W	W	W	W	w	w	W	w	w	....	w	....	......	21
W	W	W	W	W	W	w–a	w	W$_{14}$	w	W	....	w	w	......	22
a	a	a	w–a	a	a	a	a	a	a	a	...	a	w	a	23
W	a	a	w–a	a	a	w–a	a	w	w	w–a	....	a	....	a$_{18}$	24
W	w	w–a	a	a	a	a	w–a	w	w	a	....	....	....	......	25

* The table is based, with a few modifications, on the table in Fresenius (Wells' Translation).

COMMENTS ON SOLUBILITIES.

It should be remembered that salts insoluble in water often *appear* to be rendered soluble by forming new salts of *complex ions* with other salts; for instance, silver cyanide is insoluble in water, but forms with potassium cyanide a soluble salt, $K[Ag(CN)_2]$, (p. 29); mercuric iodide is insoluble in water but forms with potassium iodide a soluble salt $K(HgI_3)$; stannic sulphide forms a soluble sulphostannate, $Na_2(SnS_3)$, (p. 34). Many oxalates, insoluble in water, form soluble complex salts with ammonium or potassium oxalate, etc., — ferric, ferrous, cupric oxalates, etc., are instances. Students in using the table must, therefore, not neglect to consider all the knowledge of the nature of "solution" of a compound, and its dependence on other components which may be present.

Basic salts, (such as $(BiO)Cl$, $(BiO)NO_3$, etc.), usually are *less* soluble, *acid* salts *more* soluble, than are the normal salts given in the table.[1]

A few of the more common salts other than the normal salts are given in the following list, together with comments on special cases referred to in the table:

(1) Carbonic acid is only moderately soluble in water.

(2) Silicic acid may remain in colloidal solution in water.

(3) The acid salts, $KH(C_4H_4O_6)$ and $(NH_4)H(C_4H_4O_6)$, are somewhat difficultly soluble in water.

(4) Magnesium sulphydrate, $Mg(SH)_2$, is soluble in water.

(5) The double salt $Mg(NH_4)PO_4$, aq, is soluble in acids.

(6) Calcium sulphide is insoluble in, but decomposed by, water. The sulphydrate is soluble.

(7) Calcium acid carbonate is soluble in water but unstable.

(8) Calcum acid phosphate, $Ca(H_2PO_4)_2$, is soluble in water.

(9) Native or strongly heated aluminium oxide is insoluble in acids.

(10) Strongly heated chromium oxide is insoluble in acids.

(11) See Smith, p. 729, in regard to the chromium chlorides.

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[1] The ferric and chromic carbonates referred to in the table are *basic* carbonates.

(12) Mercuric sulphide is soluble only in aqua regia.

(13) *Cuprous* salts are oxidized by the air and more readily by nitric acid to cupric salts. The chloride, bromide, iodide and sulphide are the most common and are very difficultly or insoluble in water, but soluble in nitric acid as cupric salts.

(14) The basic acetate of copper: W–A.

(15) The basic chloride of bismuth or bismuth "oxychloride," $BiOCl$ is soluble in acids.

(16) The basic or "sub" nitrate of bismuth is soluble in acids.

(17) The basic chloride of antimony or "algaroth powder" is soluble in acids.

(18) Potassium antimonyl tartrate, or "tartar emetic," $K(SbO)C_4H_4O_6$ is soluble in water.

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